

U. S. MINES BUREAU
DEPARTMENT OF THE INTERIOR

FRANKLIN K. LANE, SECRETARY

BUREAU OF MINES

VAN. H. MANNING, DIRECTOR

ELECTRODEPOSITION
OF GOLD AND SILVER FROM
CYANIDE SOLUTIONS

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no. 150

ENGINEERING
ENGINE STORAGE

BY

S. B. CHRISTY



WASHINGTON
GOVERNMENT PRINTING OFFICE
1919



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ELECTRODEPOSITION OF GOLD AND SILVER FROM CYANIDE SOLUTIONS.

By S. B. CHRISTY.

INTRODUCTION.

This report on the electrodeposition of gold and silver from cyanide solutions represents work that has occupied my time at intervals during the past 20 years. The investigation has been carried on simultaneously with my duties as professor of mining and metallurgy of the University of California.

During this long investigation I have been assisted in the details of the work by a number of my former students, acting in turn as assistants. Particular mention in this connection is due W. H. Hilton, who graduated in 1900; C. T. Dozier, 1902; N. C. Stines, 1905; H. N. Herrick, 1907, and L. C. Uren, 1911.

It is impossible to publish full details of the many thousands of experiments performed. Effort has been made to present only the essential data. Wherever possible, the results of the experiments have been expressed in diagrammatic form by curves showing the relation between the simultaneous variables of the experiments.

It is necessary to show, as nearly as may be, the state of the art. This is difficult because of the meager literature on electrodeposition in the cyanide process; hence resort must be had to the specifications and claims of patents, most of which seem never to have been applied on a working scale. Such information consequently can not be taken at its face value. Expressing the essential ideas evolved in such specifications is no easy task. Clearly, in quoting from patent records it is not feasible to enumerate all of the specifications or the claims allowed the inventors. A statement of the chief contributions to the art in the patent cited must suffice. Legal details, of course, must be obtained from the original patent.

In the study of patent literature, when one compares the ardent hopes of the inventors with the results realized from their efforts, it becomes clear that in the development of an art no one man con-

tributes everything. Each subsequent inventor stands on the shoulders of the one who has gone before. It is only through the summation of the contributions of many inventors that the art as a whole prospers.

On October 19, 1887, a British patent was granted to McArthur and Forrest for the use of dilute cyanide solutions for treating gold and silver ores. The rapid extension of this process, in various forms, all over the world, has almost revolutionized the treatment of ores containing precious metals. It is a remarkable fact, however, that long before this patent was granted there was issued, on February 5, 1867, to J. H. Rae, U. S. patent 61866, for an electrocyanide process. Thus a method of electrodeposition from cyanide solutions used for treating ores was invented 20 years before the McArthur and Forrest patent was granted, although the process did not come into general use.

On May 24, 1889, U. S. patent 403202 was granted to McArthur and Forrest for the use of zinc shavings for removing gold and silver from cyanide solutions. The use of finely divided zinc is still the standard method for recovering gold and silver from cyanide solutions. Since this patent was granted, many attempts have been made to replace the precipitation upon the zinc by methods of electrodeposition. It is the purpose of this report to give an outline of some of these methods, as well as to show the relative advantages and disadvantages of the zinc and the electrical methods of recovering gold and silver from cyanide solutions.

PROCESSES OF ELECTRODEPOSITION.

Processes of electrodeposition may be divided into two classes, according as the action takes place, in the presence or in the absence of the pulverized ore itself.

ELECTRODEPOSITION IN THE PRESENCE OF THE ORE PULP.

All the processes of this type hitherto invented require keeping the ore pulp in motion by mechanical agitation. This is necessary, because otherwise the electrical resistance would be too great and because the metal would be deposited in filamentary form between the ore particles and would be difficult to recover.

PATENTED PROCESSES.

The first of these processes was that of J. H. Rae, previously mentioned. The patent discloses the treatment of pulverized ore in a vessel containing the ore together with a solution of cyanide of potassium. In the vessel was provided a metallic agitator which acted as

an anode and kept the ore in suspension. The gold and silver were precipitated on a plate cathode suspended in the solution above the anode. Some time in the seventies a number of experiments were made with such a process in a modified form in San Francisco with ores from Virginia City. The experiments were conducted in an amalgamating pan, the agitator being connected with one pole of the battery and the quicksilver with the other pole. When these experiments were made, it is reported that an alternating current was used, although the inventor expressly states that a direct current should be used. The results obtained were claimed to be slightly better than those with plain amalgamation, but were not enough better to warrant continuing the process.^a

On November 3, 1891, a patent (U. S. patent 162535) was granted to the celebrated Prof. William Crookes, of London. This patent was for an electroamalgamation process, by which the ore was to be suspended in a solution containing a soluble salt of mercury, such as sulphate, nitrate, or cyanide. The patent claimed that when suspended ore was submitted to the action of an alternating current of electricity the gold was rapidly amalgamated. I do not know whether this process has ever been tried commercially, but from my own incomplete study of it I do not think that it is likely to be successful. Other and more recent patents are the following:

H. F. Edwards, U. S. patent 518543, April 17, 1894.—An amalgamating device consisting of a vessel containing carbon anodes and mercury cathodes. The solution consists of cyanide of potassium and ferrous oxide. The use of ferrous oxide with cyanide is enough to put this process out of consideration.

Paul Danckwardt, U. S. patent 526099, September 18, 1894.—A process for extracting gold and silver from ores. The appliance consists of concentric drums, either the outer or the inner one of which is made to revolve, either the outer or the inner serving as an anode or a cathode. The suggested use of alkaline sulphide in connection with cyanide of potassium seems entirely out of place; and no better mechanical devices could be found for scouring the precipitated metal from the cathodes.

Pelatan and Clerici were granted three United States patents as follows: No. 551648, December 17, 1895; No. 553816, January 28, 1896; and No. 568099, December 22, 1896. These patents all disclosed cast-iron or steel agitators which acted as anodes, and amalgamated copper plates or a bath of mercury which served as the cathode. They differed from one another merely in the mechanical disposition of the agitator. The first patent showed an agitator of horizontal axis, the second one of vertical axis. The agitator described in the

^a Julian, H. F., and Smart, Edgar, Cyaniding of gold and silver ores, 1904, p. 143.

third comprised a belt made of steel with attached arms, so that when the belt was moved by rollers, the stirrers were carried over the surface of the mercury so as to agitate the pulp continuously, the operation being carried on in the presence of a cyanide solution. Experiments on a working scale with this process were conducted by D. B. Huntley in the Delamar mine, in Idaho, and I learn from him that extractions of more than 80 per cent were obtained; but I understand that none of these methods is now in use. The chief objections were the large amount of power used in fine grinding, and the scouring of the cathode. The process was replaced by cheaper leaching methods.

E. Motz, U. S. patent 582077, May 4, 1897.—This covers an electrolytic, rotated drum. The ore and pulp are mixed.

B. Becker, U. S. patent 588740, August 24, 1897.—The appliance consists of a conical tank for agitation from below by a centrifugal pump. A part of the overflow passes into a cylindrical tank having a conical bottom and containing radial or concentric vertical anodes and cathodes. The coarse gold is supposed to be amalgamated upon the sides of the first or agitating tank, and the dissolved gold, electrically precipitated, is recovered in the second tank. Circulation is controlled by suitable valves so that only the finest material passes over to the second tank for electrodeposition.

H. S. Badger, U. S. patent 635544, September 19, 1899.—Electroamalgamating barrel.

L. E. Porter, U. S. patent 639766, December 26, 1899.—Electrolytic barrel.

C. P. Tatro and George Delius, U. S. patents 640717 and 640718, March 27, 1899.—Apparatus and process.

W. Witter, U. S. patent 641571, January 16, 1900.—Cyanogen halide produced by electrolysis used later with pulp.

N. L. Turner, U. S. patent 653538, July 10, 1900.—Concentric electrodes in tank.

A. J. Irwin, U. S. patent 689674, December 24, 1901.—An endless metallic belt, as anode, supporting the pulp. The cathodes are above.

H. R. Cassel, U. S. patents 694349 and 694350, March 4, 1902.—Process and apparatus. The process comprises electrolysis of the pulp with salt, followed by the use of cyanide, to extract gold and silver.

F. T. Mumford, U. S. patent 706436, August 5, 1902.—The pulp is contained in an amalgamating cylinder of copper-lined steel. The anodes are of carbon.

W. H. Adams, jr., U. S. patent 745742, December 1, 1903.—A tank is provided having a conical bottom and an agitating device. No claims are made for any electrolytic device, but one is disclosed in the

specifications. On account of the lack of proper means for circulating the electrolyte between the inclined electrodes the process would probably be ineffective.

Ernest A. Fahrig, U. S. patent 756223, April 5, 1904.—A complicated system of agitating pulp in a series of inclined electrodes placed in a tower down which the muddy solution falls. The construction is such that an electrically efficient process seems impossible, scouring and other interferences being sure to take place. An apparatus so arranged is not easily constructed or adjusted.

E. L. Oliver, U. S. patent 784120, March 7, 1905.—An apparatus for cyanide-pulp treatment. A cylindrical tank having a conical bottom contains vertical cathodes of copper plate in electric contact with a horizontal tube containing mercury, in such a manner as to allow the mercury to spread by diffusion over the plate as the gold and silver amalgam form upon it. The anodes first specified were $\frac{1}{8}$ -inch sheet-iron plates, but these were afterwards changed to rods of Acheson graphite. The pulp was agitated by compressed air which entered at the center of the conical bottom and forced the ore up through a central pipe, causing it to spread out in the solution and fall between the electrodes. This process was introduced on a working scale at the North Star mine in 1903 and was continued in use there until 1906, during which time more than \$200,000 in bullion was recovered at a profit.^a The gold amalgam was recovered in a stronger cyanide solution by changing the cathodes into anodes (after U. S. patent 643096, S. B. Christy). The process gave good results for the treatment of low-grade tailings. An actual recovery of about 75 per cent was claimed. The difficulty in the operation of the process was that the copper plates and the quicksilver held back valuable metal. There was also considerable gold left on the anodes, particularly when the anodes were of iron. Many of the anodes assayed \$70 per ton, and even as high as \$200 per ton. Probably, also, there was a considerable loss of quicksilver. The Acheson-graphite anodes worked very well with tailings; but when an attempt was made to treat sulphide concentrate, sulphates formed and rapidly oxidized the graphite rods which soon were converted into a black mud. As long as sulphates were absent the rods were hardly acted upon. The process of precipitation at the North Star mine has since been replaced by C. H. Merrill's zinc-dust process.

W. A. Hendryx, U. S. patent 785214, March 21, 1905.—An apparatus for the extraction of metals from ores. The apparatus disclosed in the patent shows a vertical cylindrical tank with a conical bottom containing a central tube, in which is placed a revolving screw agitator which discharges the pulp in a continuous stream at the

^a Swaren, J. W., Historical notes on the air-lift agitator: Min. and Sci. Press, vol. 103, Sept. 30, 1911, pp. 410, 411.

top over a slightly conical deflecting apron so as to expose the pulp in a thin film to the action of the air. The pulp then descends through a series of electrodes inclined at a slight angle. The anodes are of carbon and the cathodes are of thin sheet lead.

W. A. Hendryx, U. S. patent 836380, November 20, 1906.—An ore-treating process which incidentally required the electrolytic apparatus previously described. The process was introduced in a number of places, but to the best of my knowledge the electrical part has been abandoned and the apparatus is now in use only as an agitator.

J. A. Comer, U. S. patent 833999, October 23, 1906.—A patent applying chiefly to the handling of pulp by compressed air. The electrical part of the device embraces nothing novel.

E. J. Garvin, U. S. patents 809939, January 16, 1906, and 822940, June 12, 1906.^a—The apparatus consists of a cylindrical agitator having a conical bottom and containing a small, inverted, floating cone in the center and a small funnel-shaped hopper at the top. The pulp is made to circulate by a centrifugal pump from the bottom of the conical tank over a series of amalgamation plates, electrically connected, which are employed for amalgamating any coarse gold. The pulp then flows through the hopper, down through the agitator, and back through the pump.

The upper part of this apparatus contains nearly clear water that has been allowed to by-pass over the top of the agitator to the electrical precipitation device, which is contained in a rectangular box with a cylindrical bottom. At the bottom of the cylinder is placed a small quantity of quicksilver; and two anodes of sheet iron are connected on either side of the cathode. This cathode consists of a link belt, made of horizontal copper strips, which moves slowly with its lower end submerged in quicksilver, thus keeping the surface amalgamated. The solution passes underneath the first anode, up through the lattice belt cathode, and thence down and out. By means of suitable valves, clear or nearly clear water passes through the precipitation tank. The coarse gold is supposed to be caught on the amalgamated copper plates on the top of the box, and the dissolved gold on the copper-belt cathode of lattice work.

Actual working results by this process are not given in the description, and seemingly it would be difficult and expensive, with this apparatus, to get sufficient area for effective precipitation. Whether it would be possible to prevent mechanical loss, either of the quicksilver or of the gold, from the cathode is perhaps questionable, especially as the descriptive circular states that the liquor flowing into the precipitation box is not always clear, but is usually somewhat turbid. The company at Portland, Oreg., formed for operating the process is said to have abandoned it.

DIFFICULTIES OF RECOVERING GOLD AND SILVER FROM CYANIDE SOLUTION
IN PRESENCE OF ORE PULP.

The idea of recovering gold and silver from cyanide solutions in the presence of the ore pulp appears at first sight attractive, as it offers a means of doing away entirely with the great difficulties of filtration and decantation; but all processes founded on this idea have to overcome other obstacles. The first difficulty is that the electrical resistance of a bath containing a large number of non-conducting particles, such as quartz, is greatly increased over that of a clear solution. A second is that the deposited metal is rapidly stripped from the cathodes by the scouring action of the moving ore particles. Such mechanical abrasion causes serious loss. When the cathodes are of mercury or amalgamated copper, a third difficulty results from the surface tension of the mercury.

I contended with this difficulty in experiments made in June, 1889. In these experiments I used as an anode a platinum dish containing roasted pyritic ore that assayed 3.38 ounces gold and 2.63 ounces silver. The dish contained, besides the ore, a 10 per cent solution of cyanide of potassium. The battery used consisted of several dry cells, and the current was 3 milliamperes. The time was 20 hours. I found that a loosely adherent black film formed on the amalgamated copper cathode. The film was easily shaken off into the ore below. The extraction, by difference, was 86.7 per cent. I repeated the same experiment the next day, using as before a platinum dish as an anode, with a 10 per cent solution of cyanide of potassium, and above the ore I placed a small flat porcelain dish (diameter 40 mm.) containing mercury, into which was inserted a graphite rod connected with the negative pole of the battery. The gold and silver and a little copper came down on the mercury in little hair-like particles of about the size and shape of the upper part of an exclamation point (!). They stood all over the surface of the mercury in an erect position like quills on "the fretful porcupine," being buoyed up by bubbles of hydrogen; and owing to the surface tension of the mercury amalgamation of these particles was difficult. Violent agitation would sweep the particles completely away from the mercury surface, whereas gentle agitation would sometimes cause them to amalgamate.

The experiments demonstrated that there are serious difficulties connected with recovering gold and silver from cyanide solutions in the presence of the moving ore pulp. Although a fairly good recovery by the method mentioned is not impossible, a really satisfactory method has not yet been devised.

In confirmation of these views the experiments of Rose^a may be quoted. Rose found that with cathodes of mercury or amalgamated copper, and with a current density greater than 0.01 ampere per square foot, a part of the gold came down as a black scum floating on the surface of the cathode in such a form that it could be brushed off with a feather. In the successful experiment with amalgamated copper cathodes there were used 0.7 volt, 0.01 ampere per square foot, 0.082 per cent KCy, and a gold content of 20 ounces per ton. With a lower density the plate remained bright, but the precipitation was extremely slow. In one test, in which mercury alone was used, and with a density ranging up to 0.027 ampere per square foot, less than 1 per cent of the gold appeared in the form of the black scum. With denser currents fully half the gold came down in the form of this scum, which could not be amalgamated except by the use of sodium amalgam. When amalgamated copper was used as the cathode, the copper dissolved in the cyanide, in spite of the current, and caused the destruction of cyanide. Hence, in view of the high cost of mercury and copper, and the difficulty of removing the gold from the copper, the methods requiring mercury or amalgamated copper as cathodes do not seem to have a bright future.

ELECTRODEPOSITION OF GOLD AND SILVER FROM CLEAR CYANIDE SOLUTIONS.

Clear solutions are obtained by either decanting or filtering the ore-bearing solutions, so that only clear solutions containing gold, silver, and possibly other metals, as double cyanides, have to be treated. In spite of the difficulties and expense of decantation and filtration, these steps seem to be necessary for satisfactory results with either electric precipitation or zinc precipitation. However, before going into a critical study of methods, two questions should be answered, namely, What is the valency of gold in cyanide solutions? At what voltage are metals best precipitated from cyanide solutions?

VALENCE OF GOLD IN ELECTROLYSIS OF CYANIDE SOLUTIONS.

It is generally admitted that the gold in cyanide solutions from ore treatment is monovalent, as KAuCy_2 , but there seems to be a general assumption that in electrolysis gold is always trivalent. In Foster's electrical engineer's pocketbook^b the atomic weight of gold is wrongly given as 195.7, and that of silver as 107.11. Gold is plainly stated to be trivalent, and the amount precipitated per ampere-hour is given as 2.4512 grams, and the amount of silver precipitated per ampere-hour is given as 4.0248 grams.

^a Rose, T. K., The electrical precipitation of gold on amalgamated copper plates: *Trans. Inst. Min. and Met.*, London, vol. 8, 1900, p. 369.

^b Compiled by R. S. Woodward, Jr., and G. S. Miller, Jr., 1910, p. 1230.

Roeber^a does not commit himself on the valence of gold, but gives the reader a free choice among three values. Roeber's article is one of the best short statements of modern electrochemical theories. His data in regard to silver and gold are as follows:

Atomic weight of silver, 107.93; valence 1, ampere-hour 4.025 grams.

Atomic weight of gold, 197.2; valence 3, ampere-hour 2.451 grams; valence 2, ampere-hour 3.677 grams; valence 1, ampere-hour 7.35 grams.

“Hütte.” Taschenbuch für Eisenhüttenleute (1902 edition) gives for silver: Atomic weight, 107.7; valence 1, ampere-hour 4.0269 grams. The values for gold are: Atomic weight, 196.2; valence 3. ampere-hour, 2.4453 grams.

Steinach and Buchner^b give the following values: Silver, monovalent, ampere-hour 4.026 grams; gold, trivalent, amper-hour 2.445 grams.

Keith^c says that gold is trivalent in cyanide solutions.

According to the International Atomic Weights Committee^d the atomic weight of silver is 107.93, with a possible error not greater than ± 0.01 , and the atomic weight of gold is 197.2, with a possible error not greater than ± 0.1 . These values being assumed to be correct, if gold is monovalent, for every grain of silver precipitated by a given current 1.837 grams of gold should be precipitated by the same current, and if gold is trivalent, for each gram of silver precipitated there should be precipitated only 0.612 gram of gold.

Of course gold is capable of reacting in at least two cyanide compounds— KAuCy_2 and KAuCy_4 —the former of which is monovalent and the latter trivalent. In estimating the electrical efficiency of cyanide precipitations, it is absolutely necessary to know which of these values to choose for the reactions that take place. To investigate this matter I prepared three separate solutions, as follows: No. 1 containing 250 mg. of silver as nitrate, No. 2 containing 250 mg. of silver as KAgCy_2 and 150 mg. of free KCy , and No. 3 containing 100 mg. of gold as KAuCy_2 and 150 mg. of free KCy . The anodes and cathodes in solutions 1 and 2 were both of pure silver. In solution 3 they were of pure gold. Three cells were thus set up in series with a storage-battery cell of 2 volts, and after a period of 1 hour and 50 minutes all the electrodes were weighed. The following results were obtained:

^a Roeber, E. F., Standard handbook for electrical engineers, 1908, 1,285 pp.

^b Steinach, Hubert, and Buchner, Georg, Die galvinischen Metallniederschläge, und deren Ausführung, Berlin, 1890, 258 pp.

^c Keith, N. S., Electrolysis of gold: Jour. Inst. Elec. Eng., vol. 24, 1895, pp. 236-260.

^d Clarke, F. W., Seubert, K. E., and Thorpe, J. E., Report of the International Committee on Atomic Weights, 1903, p. 5.

Experiment 1. The anode (A) lost 45.23 mg., and the cathode (B) gained 43.22 mg. The silver came down in fine crystals, and a small proportion of these was unavoidably lost in weighing, which accounts for the low value obtained.

Experiment 2. The silver anode (C) lost 45.12 mg., and the cathode (D) gained 43.78 mg.

Experiment 3. The gold anode (E) lost 81.52 mg., and the cathode (F) gained 76.69 mg. It will be noticed that the gain in each test was slightly less than the loss, even in experiment 1, in which there was mechanical loss in weighing the cathodes.

Let us compare the gain of the gold cathode F with that of the silver-nitrate cathode B. Dividing F by B, we have 1.774, and comparing the gain of the gold cathode F with that of the silver cathode D, both values being in cyanide of silver, we have $\frac{F}{D} = 1.75$.

However, as there might be a slight loss in weighing the cathodes, it might be nearer the truth to compare the losses of the anodes rather than the gains of the cathodes. First let us compare the gold loss from anode E with the silver loss from anode C, both in cyanide solutions. If we divide E by C the quotient will be 1.807 instead of 1.837. Supposing the metal to be monovalent, if we divide E by A we have 1.802 instead of 1.837.

It must be evident therefore that in aurocyanide of potassium solutions the gold acts practically as a monovalent metal. That less gold is precipitated than is dissolved in cyanide solutions is probably due to the presence of free cyanide of potassium. It is necessary however to have a certain excess of cyanide, as if there is no excess, AuCy_2 forms on the anodes.

Iron is sometimes trivalent and sometimes bivalent, and it is possible that similarly gold may be both monovalent and trivalent. It is well known that gold does exist as potassium auricyanide, but it appears that the aurocyanide salt is much more stable, the auricyanide tending to break down into the aurocyanide. However, there seems to be no reasonable doubt that in estimating the electrical efficiency in precipitation processes the gold should be considered as monovalent.

VOLTAGES AT WHICH THE METAL IS COMPLETELY PRECIPITATED FROM CYANIDES.

This is a subject about which little has been published. Friedenberg^a claims that the precipitation is as follows:

K_2HgCy_4 complete at 1.6 volts.

KAgCy_2 complete at 1.7 to 1.8 volts.

^a Friedenberg, Ztschr. Phys. Chem., Bd. 12, 1891, p. 97.

KAuCy₂ complete at 1.9 volts.

K₂CuCy₄ (with $\frac{1}{2}$ to 1 part KCy) at 2 volts.

KCuCY₂ (with 10 to 15 parts KCy) at 2.5 volts.

Some precipitation is possible at lower voltages than these. Theoretically, complete precipitation would require an infinite voltage, but what is meant by the author quoted is precipitation sufficiently complete for quantitative purposes. From my experience I consider the voltage given for copper entirely too low. Experience shows that much depends on the amount of free cyanide and other salts present.

The figures cited are to be regarded only as lower limits. The author states that the precipitation is slow at these voltages and prefers to use 2.5 volts for gold. The figures explain the low results obtained in the experiments with the Keith process in which an average voltage of only 0.75 was used.

SIEMENS & HALSKE PROCESS.

In 1888 Wernher von Siemens first applied for patents (Heirs of E. W. von Siemens, U. S. patent 601068, Mar. 22, 1898) for his process of electrical precipitation which seems not to have been introduced on a working scale until 1893. The process had previously been patented in the Transvaal under date of July 7, 1892, patent 397. The patent covers both the method and the apparatus, according to the patent laws then in force. The precipitation method claimed is as follows: "A method of extracting gold from a weak cyanide solution, which consists in circulating the solution over anodes of iron and cathodes of lead. Said cathodes being formed of thin plates arranged at short distances apart, and have from 9 to 10 square feet of surface for each ton of solution in contact with them. Said solution while in motion is subjected to an electrical current of from $3\frac{1}{2}$ to 4 volts and 0.5 to 1.5 amperes per square meter of cathode surface substantially as set forth." It will be observed that the claims allowed are not general but are much restricted in their nature.

The Siemens process was first introduced in South Africa through the agency of Charles Butters, and although the patent shows a centrifugal pump as the means of continuously circulating the solution through the deposition box, this was soon abandoned and the process was applied by constructing long boxes to allow the gold and silver to be deposited sufficiently by a single flow through the box. The anodes were of iron, and were placed 3 inches from the cathodes, which were made of thin strips of lead. As soon as 2 to 12 per cent of the gold, or on an average 7 to 8 per cent, had been deposited on

the lead cathodes, the lead strips were taken out from the cells, melted down, and cupelled.

This process, popularly known as the "Siemens & Halske process," was used for a long time in the Transvaal in competition with precipitation by zinc shavings, and was fairly successful there under the management of Mr. Butters. However, after he left the Transvaal, the method was gradually replaced by precipitation by zinc shavings, the latter method having been greatly improved. For some time the Siemens & Halske process has been substantially abandoned in Africa. In a modified form, mentioned later, electrical precipitation is still used by Mr. Butters in several of the mines under his management.

One difficulty with the Siemens & Halske process was the large size of the box necessary for effective precipitation. Mr. Butters told me that when he first constructed the cells some of his English friends asked, "Are you constructing stalls for horses?" The cells were large enough to have been used for that purpose. One of the reasons for the large size was the necessity of avoiding short circuits. These were liable to be encountered owing to the fact that the anodes, in the presence of sulphates and chlorides, contained in the solution, soon became coated with warty growths of hydrate and hydrated carbonate of iron and prussian blue. Hence a 3-inch space was left between the anodes and the cathodes. The maximum daily capacity was not usually more than 5 tons of solution treated to each box holding 1 ton of solution, and the volume treated was usually much less.

There have been many descriptions of the Siemens & Halske process, but most of them omit some detail necessary for calculation of the electrical efficiency. The most complete description of the essential details of the process that I have been able to find is that by Richards.^a

There were four deposition boxes, each 30 feet long by 4 feet 9 inches wide and 3 feet deep. Each box contained 110 iron anodes and 110 cathodes formed of bags containing 5 to 10 pounds of lead shavings the extent of the surface of which is problematical. The tanks were electrically coupled in series, 2.5 volts being required for each. The current was 200 amperes. Each box held about 14 tons of solution, or, allowing for the electrodes, 10 to 12 tons, so that the capacity of a box holding 1 ton of solution would have been 4 to 5 tons a day. The heads assayed 80 and the tails 15 grains gold. Hence, only about 81.5 per cent of the gold content, weighing 3,250 grains (0.464 pound or 0.21 kilogram), was precipitated at this rate of flow per day. Prof. Richards comments as follows:

That this is an insignificant amount for the current passing (200 amperes), which should theoretically deposit 34.56 kilograms in each box, is patent to the

^a Richards, J. W., The cyanide process for the treatment of gold ores: Jour. Franklin Inst., vol. 143, February, 1897, p. 96.

electrometallurgist, the yield being only 0.6 per cent, but it must be remembered that the extraordinarily dilute solution used will not yield up its gold any faster and that it must be electrolyzed slowly to get any sort of correspondence between the power used and the gold obtained.

Under the conditions of the Siemens & Halske process this statement is true, but, as shown later, under the right conditions better results can be obtained.

If we assume as correct that 7.35 grams of gold should be precipitated in 1 ampere-hour, it follows that 200 amperes should precipitate 1,470 grams each hour, or in 24 hours there should have been precipitated 35.28 kg. instead of 0.21, showing that the efficiency was only 0.59 per cent, which is essentially the same as that of Prof. Richards, who seemingly used a different constant. The gold recovery also is rather low, there being a reduction only from \$4.26 to \$0.64 per ton.

Julian and Smart's excellent book,^a giving details of the Siemens & Halske method of electrical precipitation, has been carefully examined to see whether it presented data that could be used in calculating the electrical efficiency of the process. Although Table 31 contains 18 columns of data, it is not complete enough for a reliable calculation of the electrical efficiency.

However, by making some assumptions, approximations may be possible.

Thus a high precipitation is cited as being obtained at the Croesus works where seemingly the gold content is said to be reduced from 48 grains to a trace. However, the authors do not state the current density per square foot of cathode surface, but it probably was not higher than that cited for other operations, namely, 0.04 ampere per square foot. Only one precipitation box, containing 38.8 tons of solution, was used, 50 tons being treated in 24 hours. On the basis of a 1-ton box the rate would be 1.29 tons of solution per 24 hours. The cathode area is given as 7,680 square feet. If we assume the current density to be 0.04 ampere per square foot we shall have 307 amperes, or 7,368 ampere-hours, a day. Precipitation should then be at the rate of 7.35 grams of gold per ampere-hour, or 54.155 kg. of gold. The heads are said to have contained 48 grains and the tails a trace. If we assume all of the gold, 48 grains per ton, to have been precipitated, the recovery for the 50 tons of solution would be 2,400 grains, or 0.156 kg. of gold actually precipitated. Dividing 0.156 by 54.155 gives only 0.288 per cent as an electrical efficiency. Hence, although the recovery is rather high, the capacity per ton of box capacity is only 1.3 tons of solution a day, and the electrical efficiency is less than 0.3 per cent, which is one-half that calculated by Richards.

^a Julian, H. F., and Smart, Edgar, Cyaniding gold and silver ores, 1904, p. 143.

The figures as presented by Julian and Smart for the May Consolidated plant may next be considered. Two results are given—the one covering the solution coming from the sand tank, and the other covering the solution from the slimes. In the sand tank 6 boxes were used, containing 133.2 tons of solution. These treat 300 tons a day. Consequently the capacity on the basis of a 1-ton box is 2.25 tons a day. The cathode surface is not given. If we assume it to be the same as the anode surface, 13.824 square feet, with a current density of 0.04 ampere, we shall have a total of 553 amperes, or in 24 hours, 13,271 ampere-hours. This current should precipitate 97.542 kg. of gold. As a matter of fact the head solution assayed 120 grains of gold per ton and the tail solution 18 grains, or there was precipitated 102 grains per ton. For the 300 tons, with the weights converted to kilograms, there was precipitated 1.982 kg. of gold, or the electrical efficiency was 2.03 per cent, according to the data given and the assumptions here made. But it is altogether probable that the cathode surface was much larger than that of the anodes. Hence the efficiency would be much less than that stated. The precipitation is rather high, being over 93 per cent, but the capacity is low, being one-half of what I obtained with my experiments at Bodie.

Considering the May Consolidated slime plant, we find that the solution was treated in four boxes, containing 181 tons, in which 320 tons was treated each day. At this rate a 1-ton box would have a capacity in 24 hours of 1.73 tons, a lower rate than was obtained from the sand solution. There was 16,892 square feet of anode surface. The cathode surface is not given, but was probably larger than that of the anode surface, and if the surface of each be assumed to have been the same, with a current density of 0.04 ampere, the daily current of 16,220 ampere-hours thus obtained should have precipitated 119.22 kg. of gold. As a matter of fact the head solution contained only 24 grains of gold and the tail solution 2.4 grains. There was actually recovered, per ton, 21.6 grains of gold, or, from 320 tons there was precipitated 0.448 kg. of gold. This when divided by 119.2 gives only 0.376 per cent electrical efficiency. If, as is probable, the cathode surface was larger than the anode surface, the electrical efficiency would be still lower.

MOLLOY PROCESS.

The following description of the Molloy process is taken from Julian and Smart:^a

This process was patented in the Transvaal in 1892 by B. C. Molloy, where it was employed for some months. It consists in passing the gold-bearing solution over a surface of mercury in which sodium was continuously deposited.

^a Julian, H. F., and Smart, Edgar, Cyaniding gold and silver ores, 1904, p. 158.

An ingeniously devised apparatus was employed which consisted of a large shallow tray covered with mercury, down the center of which was a narrow compartment, with sides that dipped slightly into the mercury. In this compartment was placed a strong solution of sodium carbonate which was electrolyzed, the mercury at the bottom being the cathode, and the anode was of peroxidized lead. As the sodium deposited and accumulated in the mercury within the compartment it diffused to the mercury on the outside, over which a constant stream of gold-bearing solution was kept flowing. The gold-bearing molecules dissolved as they came in contact with the sodium amalgam surface, were decomposed, and gold amalgam formed.

The process was ably developed by Dr. A. Simon, who employed it on a working scale in the treatment of tailings on Witwatersrand in 1892-93.

The weak point of the process lies in the difficulty of getting a sufficiently large electrode surface for the solution to come in contact with, without unduly increasing the amount of mercury handled. Thus, if the area of a surface required to reduce a 5 dwt. solution down to 1 dwt. was 1, that to reduce a 1 dwt. solution down to 5 grs. would have to be somewhere about 25 with the same rate of flow, showing how enormously the area has to be increased as the solution becomes impoverished. This difficulty may, however, be got over, to some extent, by agitating the solution rapidly over the sodium amalgam surface as it flows, by mechanical means. The efficiency of sodium amalgam as a precipitant is small, but when employed in a dilute state, as in the Molloy process, it compares favorably with the electrical precipitation processes of to-day. Sodium amalgam is said to act on KCy in solution forming complexes, but in dilute working solution this action is inappreciable.

I have obtained good precipitation by this method so long as the capacity was limited, but the moment it was pushed, the extraction fell off. Of course, all the objections to the use of mercury apply. The process seems to have been abandoned.

VARIOUS OTHER PATENTED PROCESSES.

Johannes Pfleger, British patent 16737, September 6, 1895.—The inventor uses cathodes composed of shavings, wire, powder, or shot and presenting a large surface. He prefers iron-wire cloth of $\frac{1}{16}$ -inch to $\frac{1}{8}$ -inch mesh, but finds that 10 to 30 wires per linear inch answer the requirements. The specifications show a deposition box containing an interior compartment filled with wire cloth, and provided with transverse partitions so arranged as to force the solution alternately down and up through the wire cloth. On either side of this interior compartment are two outer compartments separated from the inner one by diaphragms. Outside the diaphragms the vessel contains a 1 to 5 per cent solution of soda, and in this latter solution zinc-plate anodes are placed, forming with the cathodes a galvanic cell. This cell, when the anodes and the cathodes are connected, forms a circuit which, it is claimed, will rapidly cause the metal to be deposited on the wire cloth, and the zinc plates to dissolve in the soda solution. It is evident that in this apparatus no exterior electrical power is used. The electromotive force available is limited to 0.6 to 1 volt.

Julian and Smart ^a give the capacity of a 1-ton box as 16 tons per 24 hours. The process seems to have been abandoned.

Oscar Froelich, U. S. Patent 556092, March 10, 1896.—Lead cathodes and carbon anodes are used. The current density is 6 amperes per square yard. The solution is seemingly clear.

Rudolf Keck, U. S. Patent 566986, September 1, 1896.—Clear solution, lead anodes, and aluminum cathodes.

Emile Andreoli, U. S. Patent 568724, October 6, 1896.—An apparatus for the electrical deposition of gold and silver in a tank provided with one or more anodes and a series of amalgamated cathodes. Each cathode consists of a previous skeleton of knit-wire plates upon a layer of mercury in the bottom of the tank, into which the cathode dips. This patent discloses the use of peroxidized lead as anodes. The solution used is clear. Anodes are contained in compartments separated from the cathodes by permeable membranes. According to the description, only two anodes are used. The inventor places the anodes on the sides of the tank. The cathodes dip into a bath of mercury at the bottom. The use of the network of wire gauze is specified. The diaphragms are made preferably of porous asbestos or kieselguhr (infusorial earth) porcelain, but woven tissues stretched on frames may be used. It is specifically stated that the porous partitions may be omitted, and that the cathodes may be placed crosswise, one perforated anode being used for 12 to 15 cathodes. The patent shows a great advance in the art, particularly the use of peroxidized-lead anodes, which is a valuable discovery. The use of the wire cloth is also good, but the process necessitates the use of a large volume of quicksilver in the bath, which is a serious disadvantage, although it is convenient in making the electrical connections. However, the process does not appear to be practicable on account of the great difficulty of removing the gold and silver from the cathodes.

Andreoli ^b has written an interesting article on the electrical deposition and recovery of gold. In this article he explains his discovery of the peroxidized-lead anode. He states that this anode was not the result of research or study, but was simply a chance discovery. His first plates were made according to the Plante method, but, at present, he prefers to use plumbeate of soda repeatedly to coat the plates with peroxidized lead. When so treated the plates are drawn, washed, and placed in a strong solution of cyanide of potassium, where, under a heavy current, they become hard and acquire a crystalline appearance. In reference to his process Andreoli states: "I was soon disappointed when I was told that no one in mining districts would care much to adopt such a process which involved too much

^a Julian, H. E., and Smart, Edgar. Cyaniding gold and silver ores, 1904, p. 120.

^b Andreoli, E. Electrodeposition and recovery of gold: Jour. Soc. Chem. Ind., vol. 16, Feb. 27, 1897, pp. 96-97.

trouble in distilling the mercury and cleaning the plates in order to recover the gold amalgamated with it." He therefore altered the process by using cathodes of iron plates, upon which the gold and silver were deposited. He then recovered the gold and silver from the iron plates by dipping them in molten lead, whereupon the gold and silver alloyed with the lead and the plates were stripped. However, the iron plates are said to have become warped by the treatment with the hot lead, so that they easily produced short circuits. The only part of the Andreoli process that has been permanently adopted is the use of the peroxidized-lead anodes.

Max Netto, U. S. Patent 573233, December 15, 1896—This process consists in precipitating silver and gold from alkali-cyanide solutions by acidulating with hydrochloric acid so as to precipitate silver chloride, separating the precipitated silver chloride by filtration from the solution, and subjecting the acid filtrate to the action of an electric current so as to deposit the gold on the cathode. The inventor regenerates the cyanide solution by the addition of caustic alkali.

Precipitation of silver and gold in the presence of cyanide of potassium by hydrochloric acid is seldom complete. If the solution is high in cyanide and low in gold no precipitation of gold occurs; but if the solution contains a small amount of cyanide and a large amount of gold and silver, a certain amount of gold always comes down with the silver.^a On account of these reasons and the cost of the acid and alkali, it would seem that the process is hardly practicable, except where acid and alkali are much cheaper than cyanide.

J. F. Webb, U. S. Patent 585492, June 29, 1897—A method and apparatus for separating precious metals from their solvent solutions. The specifications show a box containing alternate vertical columns of zinc shavings and carbon. The carbon is said to be either charcoal or coke. The solution passes down through the charcoal and up through the zinc, the first compartment containing carbon and the last one zinc. The terminal columns of carbon and zinc are connected by wire, and electrical action between the carbon and the zinc is claimed. The inventor does not, however, rely upon this connection alone, claiming that the zinc and charcoal act sufficiently without the connection. As ordinary charcoal is not a conductor of electricity, there can be here electrical action only between the coke and the zinc, and the use of an external source of current for the process can not be claimed. Practically only local action can take place.

E. Andreoli, U. S. Patent 598193, February 1, 1898—An apparatus for the electrical deposition of gold, silver, and other precious

^a See Christy, S. B., Solution and precipitation of cyanide of gold: Trans., Am. Inst. Mining, Eng., vol. 26, 1896, pp. 747-748.

metals. The inventor uses anodes of peroxidized lead acting in the presence of and in combination with the cyanide solution. The cathodes are made of perforated zinc plates.

The first great improvement over the Siemens & Halske process was the introduction of the peroxidized lead anodes discovered by Andreoli. When the lead plate was covered with a perfectly continuous film of peroxide of lead the anodes were practically unattacked by the cyanide solution, but whenever this film became broken, so as to expose the metallic lead, a white funguslike growth of hydrate and cyanide of lead formed upon the lead which was almost as destructive as the hydrate of iron that forms on the iron plate. When this action takes place, lead anodes are soon corroded and finally fall to pieces. Mercury also rots lead plates and soon destroys them. Experiments that I have made show that, in cyanide of potassium, the peroxide-of-lead anodes are practically unacted on when new, but that, in the presence of potassic hydrate, they dissolve slightly and a trace of lead comes down on the cathode.

The solubility of PbO_2 in KCy and KHO was shown in experiments made November 26, 1900. I took as an anode an old peroxidized plate from a storage battery and as a solution 0.2 per cent potassium cyanide. As a cathode I used a platinum sheet $6\frac{1}{2}$ by 8 centimeters. The weight of the platinum cathode before treatment was 18.6734 grams. When treated with a voltage of 4 volts and a current of 0.068 to 0.11 ampere for two hours the cathode of platinum, which had previously been carefully cleaned, actually lost 2 mg. in weight. This result was typical of many experiments, and the results of other experimenters show similarly a slight loss of platinum from cathodes in cyanide electrolysis. Certainly at this time no lead was deposited. To the solution was then added KHO to bring the total to 0.1 per cent free KHO . For two hours the voltage was again 4, and the current 0.171 to 0.070 ampere. The gain in weight of the platinum cathode was 0.7 mg., caused probably by deposited lead. I then added salt to make 0.2 per cent NaCl and continued the treatment for 16 hours with a voltage of 3.7 to 3.42 volts, and a current at 0.2 to 0.56 ampere. The gain in weight of the cathode was 8.2 mg. The conclusion was that dilute solutions of KCy do not alone attack peroxide of lead in two hours, but that KCy containing KHO and NaCl do attack it slightly.

Kern^a claims that peroxidized lead anodes fail, owing to the electrolyte attacking the lead through the pores in the peroxide coating, but I believe this to be more likely due to cracks in the brittle coating of peroxide caused by the easy bending of the lead within.

^a Kern, E. F., Electrolysis of cyanide solution: *Trans. Am. Electrochem. Soc.*, vol. 24, 1913, pp. 241-270.

N. S. Keith, U. S. patent 597820, July 25, 1898—A process for treating ore with a cyanide solution containing cyanide of mercury. The gold and silver are recovered from the filtered solution by passing a current of electricity of less than 1 volt through suitable anodes and cathodes upon which the metal deposits as a coating of amalgam. I saw this process in operation in the year 1898. The ores came from Cripple Creek, Colo., and were treated at Cyanide, Colo. The anodes and cathodes were both of sheet iron, and the solution passed alternately up and down between the electrodes.

EXPERIMENTS WITH KEITH PROCESS AT CYANIDE, COLO.

I am indebted to Mr. Philip Argall for the following data on the use of the Keith process. From March 31 to April 9, 15 tons of solution was used to treat 83 tons of ore, the precipitated solution being used over again. The precipitation process is of chief interest.

The precipitation was conducted in a tank 12.5 by 3 by 4 feet, having a total content of 150 cubic feet, or containing about 5 tons of solution. It treated 7 to 13 tons a day, or an average of 10 tons. That is, a 1-ton tank would have had a capacity of about 2 tons in 24 hours. The anodes and cathodes were of sheet iron 4 by 3 feet. There were 50 cathodes so that the total area on both sides was 1,200 square feet. As there were 20 amperes flowing through the box, the current density was about 0.017 ampere per square foot. The potential varied from 0.5 to 0.9, averaging 0.75 volt.

From March 31 to April 9, the solution treated was used in leaching ore. During this time the solution entering the box ran from 1.605 to 0.215 ounces of gold, and that leaving the box ran from 0.385 to 0.107 ounce. On two days it left the box richer than it entered, but as no record is given of voltage and amperes for those days there may have been a defect in the current. The best precipitation was 76 per cent (the first day); the precipitation varied from that figure to 15 per cent and less, or even to negative value.

From April 10 to 21 the solution was no longer used to treat ore, but was pumped back to a tank and allowed to flow repeatedly through the box at the rate of 10 tons per day to indicate what the precipitation process could do. In 12 days gold content of the heads was reduced from 0.135 to 0.050 ounce. The solution was treated at the rate of 2 tons a day in a 1-ton box, or of 12 to 22 pounds per 24 hours per square foot of cathode surface. As the box was 12.5 feet long and there were 51 anodes and 50 cathodes, the average distance between the electrodes was 1.5 inches. The same solution when afterwards passed only once through boxes of zinc shavings was reduced to 0.015 ounce, or about 30 cents a ton. The original solution used by Prof. Keith contained 0.19 per cent KCy and 0.66 per cent NaHO,

and the final solution contained 0.04 per cent KCy and 0.155 per cent NaHO. There was used also 12 pounds of HgO. Mr. Argall comments as follows:

During deposition a black deposit collected on the cathodes, interfering with precipitation. This deposit had to be cleaned off three times. The material collected was chiefly of a graphitic nature, oxide of mercury and gold. The gold recovered from the black mud amounted to 25.7 per cent of the total gold recovered.

The mercury appeared to be the first metal deposited; consequently, the plates from the center to the end of vat were very hard, and the amalgam was extremely difficult to remove. When I decided to make a complete clean-up and abandon the process, some 5 pounds of mercury oxide was dissolved in the solution to soften the plates, and even with this addition of mercury it took two men one week to clean 50 plates, and when they had scoured off all the deposit possible, using mercury freely in rubbing the plates, there still remained on or in the plates 41.5 per cent of the total gold recovered.^a

Recapitulation:

	Per cent.
Gold recovered as amalgam-----	32.8
Gold recovered as mud-----	25.7
Plates in 1 per cent cyanide solution-----	41.5

The cathodes were attacked and pitted somewhat. The anodes did not show much action, though a little Prussian blue appeared in places.

The result of this test led to the abandonment of the Keith process. Seemingly, the small amount of action on the anodes, which were nearly covered with a thin, hard scale of ferric oxide, was due to the low voltage used. This was always less than 1 volt. Curiously enough, the best precipitation was from a rich solution, on the first day, when the voltage recorded was only 0.5 volt. According to Mr. Argall the mercuric cyanide seemed slightly to hasten the solution of the gold, but not sufficiently to justify its use. This has been denied. Mr. Claude Vautin states that experiments in Hungary (1893-95) showed that the use of mercuric cyanide actually retarded the solution of the gold. I think that it probably retarded the precipitation of the gold.

In the light of further experience there were shown to be three serious defects in the process as conducted. First, the voltage was too low. The good results obtained upon the first day, with 0.5 volt, were doubtless due to the fact that the cathodes were of naked iron; but as soon as the cathodes became coated with gold, a back electro-motive force operated to oppose further deposition of gold. The second defect was the use of mercury, the surface tension of which increased the difficulty of precipitation. The third defect was the sluggish circulation. The difficulties of the clean-up would largely disappear in regular work, just as they do in the use of amalgamated copper plates. It would be as difficult finally to clean them.

^a This was subsequently recovered by soaking the plates in a 1 per cent KCy solution. Author.

FIRST DEVELOPMENT OF THE CHRISTY PROCESS.

When I first looked into the electrodeposition of gold and silver from cyanide solutions it seemed to me that the low ampere-hour efficiency in the Siemens process was a fatal bar to the success of electrical deposition, and I was not surprised that the process was abandoned in South Africa shortly after Mr. Butters left there. But in discussing the matter with the late Stephen D. Field, the well known electrical engineer, my attention was called to the fact that the ordinary telephone has less than 1 per cent of electrical efficiency, and yet it is one of the most successful of modern inventions. This suggestion caused me to attack the problem with renewed interest, as I thought the method might still be made effective if given more careful study. Siemens was well aware of the importance of having a large electrode area, and he especially calls attention to the importance of increasing this rather than the voltage of the bath.

I soon came to the conclusion that all electrical processes that used quicksilver, either in the liquid form or in the form of amalgamated plates, except for treating free gold, coarse enough to overcome the surface tension of the mercury, were not likely to be successful with cyanide solutions. Such processes involve the use of a large amount of expensive metal, difficult to handle without loss, and involve the danger of salivation of the workmen. Moreover, there is the difficulty, already mentioned, arising from the necessity of overcoming the surface tension of the metal. This difficulty was particularly evident in the test of the Keith process at Cyanide, Colo. There was also great difficulty in recovering the amalgam from the large area of the cathode plates necessary for a complete precipitation. I noticed, moreover, that so long as the solution contained no sulphates or chlorides the anode plates, of iron, were little acted upon, being simply covered with a thin film of ferric oxide which protected the metal from further action, although it slightly increased the resistance.

Starting with the principle that an enormous cathode surface was necessary for the rapid and complete precipitation of the gold and silver, I made a number of experiments, using sheet iron for both cathodes and anodes. I found that when the current was not too great the precipitated gold and silver adhered firmly to the surface of the sheet-iron cathode. I then removed the cathodes, two at a time, and made them anodes in a dilute cyanide solution of about 0.1 per cent, and redissolved and reprecipitated the gold electrolytically upon a piece of sheet iron covered with a thin film of graphite and vaseline. On graphiting the surface of the sheet iron I found it possible, under proper conditions, to reprecipitate the gold and

silver in a dense coherent sheet, which afterwards could be stripped in sheets ready for the mint.

On February 6, 1900, I was granted U. S. patent 643096, for "a process of progressive electroconcentration and recovery of gold and silver contained in the large volumes of dilute cyanide solution containing free alkali resulting from the extraction of gold and silver ores, tailings, and concentrates, which consists first in depositing the gold and silver electrolytically from said solution upon removable cathodes sufficiently numerous and large in area to secure efficient deposition, and second, in making said removable original cathodes successively anodes in a smaller volume of cyanide solution, and transferring and depositing electrolytically the thin film of gold and silver already distributed over a large number of said original cathodes upon a smaller number of secondary cathodes, also contained in said smaller volume of cyanide solution."

EXPERIMENTS AT STANDARD CONSOLIDATED MINE, BODIE, CAL.

In the summer of 1900 I tried this process on a small scale at Bodie, Cal. The solution treated was 0.937 short ton, having an assay value of 0.175 ounce of gold and 0.437 ounce of silver. Although the metal values were almost entirely in the gold, there was nearly three times as much silver as gold in the solution. The assay value of the head solution was about \$4 per ton, gold and silver. The average of the entire solution after treatment was only about 10 cents a ton, some assays being as low as 2 cents. All the assays were made by the company assayer, W. M. Knox. Samples of eight assay tons of solution were assayed by evaporation with litharge.

The deposition box used was 2 feet 6 inches by 4 inches by 6 inches, and held 0.4 cubic foot. It treated solution at the rate of 2 cubic feet per day, or five times its capacity, with good results, but on pushing the work beyond the capacity of the box, the value of the tailing would run up to 20 or 30 cents.

There were 27 cathodes of thin sheet iron, 4 by 5 inches; hence their exposed surface on both sides was 7.5 square feet. The current varied from 0.5 to 1.3 amperes, the cathode current density varying between 0.066 and 0.173 ampere per square foot, averaging 0.135 ampere. For a part of the time, two boxes were used, in series, as far as solution was concerned, but electrically in parallel; hence the current density was then only 0.068 ampere. The voltage varied from 0.8 to 3.6 volts. The electrodes were all placed transversely across the box and $\frac{1}{2}$ inch apart, so that the solution flowed alternately up and down the box. Alternate anodes projected above the surface of the solution and were perforated with $\frac{1}{4}$ -inch holes to allow the solution to flow through. The flow through these holes

was more rapid than usual, and I found the deposit opposite these holes to be thicker and better than elsewhere. This discovery first suggested to me the advantage of rapid circulation through previous electrodes, an idea that was developed later.

In order to preserve the anodes from corrosion they were coated with a mixture first suggested by Mr. Bettal of South Africa. This mixture consists of graphite, litharge, boiled oil, and turpentine; it is put on hot. I found that with a low current density (voltages up to 0.14 volt) the anode coating stood up well, as was claimed for it, but that as soon as the pressure was raised to 2 or 3 volts, in order to increase the precipitation, the boiled oil and turpentine were attacked, producing a vile-smelling mixture. The iron was then so attacked that the anodes had to be scraped clean.

There was considerable trouble in getting a continuous, direct-current service of a proper voltage. Alternating current was brought from a distance and was erratic, so that, although for a part of the time, direct dynamo service was available, frequent resort was necessary to a couple of large improvised Daniell cells.

THE CLEAN-UP.

The clean-up was effected in a cell that held 750 c. c. of cyanide solution, and accommodated two anodes (two cathodes from the deposition box, to be stripped) and one sheet-iron cathode, on which the gold and silver were to be precipitated. This cathode was coated with a layer of graphite and wax, put on hot, and rubbed dry with graphite, to favor the subsequent stripping of the concentrated metal. With two Daniell cells giving 1.4 volts in closed circuit, 0.200 ampere was obtained, but this fell rapidly to 0.050 ampere. The iron anodes did not appear to corrode, yet some of the metal came down ratherly loosely on the cathode which became coated evenly with silver and gold. The clean-up solution, which at first was 0.1 per cent KCy, was afterwards made 1 per cent. The cathodes from the head of the deposition box required about 1 hour for stripping, and those from the tail required only a few minutes. The cathodes from the deposition box (anodes in the clean-up box) showed no signs of pitting except in one instance when the current was left on over night. If the stripping was stopped when nearly complete the oxidation of the anodes in the clean-up box could be easily avoided, especially as clean cyanide solution free from chlorides and sulphates could be used for stripping. While the metal was partly adherent to the cathode, much of it came down as a dark, blackish-brown powder, easy to filter and to melt. In later experiments the deposition of this precipitate was avoided by proper circulation. The scrapings from the anodes of the deposition box after treating

the mill solution contained graphite, linseed oil, etc., with more or less hydrate of iron and Prussian blue; weighed about 316 grams; and carried 0.16262 gram in gold and 0.30785 gram in silver. The total clean-up resulted as follows:

Clean-up in experiments at Bodie, Cal.

	Gold, grams.	Silver, grams.
From solid metal from cathode of clean-up box	1.61678	4.14322
From metallic dust from clean-up box	1.95100	5.53900
From cyanide solution from clean-up box	.44346	.85814
From wash water from anodes in clean-up box	.14936	.36704
From various sediments from deposition box	.16362	.30785
	4.32322	11.21525

The original solution treated was 0.937 ton, which assayed 0.164 troy ounce of gold and 0.435 troy ounce of silver; hence in grams the result was as follows:

	Gold, grams.	Silver, grams.
Original content	5.11	12.70
Actual recovery	4.32	11.22
Lost in tailing solution, assay samples, etc.	.79	1.48

An 8-assay-ton charge of the tailing solution from the whole charge gave 0.005 ounce of gold per ton and 0.005 ounce of silver; that is, the tailings were worth a little more than 10 cents a ton, and there were left in the 0.937 ton of solution only 0.146 gram each of gold and silver. Hence the result was as follows:

	Gold, grams.	Silver, grams.
Original content	5.11	12.7
Residual solution	.146	.146
Difference	4.964	12.554
Actually recovered in clean-up	4.323	11.215
Losses and assay samples	.641	1.239
Loss in tailing	.146	.146
	^a .787	^b 1.385

EFFICIENCY OF DEPOSITION.

The total time of the experiments during which the current was passing was 127.5 hours. The total number of ampere-hours was 126. The weight of gold actually recovered, divided by 7.35, the weight in grams of gold that should have been deposited in 1 ampere-hour, was as follows: $\frac{4.323}{7.35} = 0.588$ ampere-hour, which should have

^a Compare with the 0.79 value given above.

^b Agrees with the 1.48 value given above.

sufficed to deposit the amount of gold at 100 per cent electrical efficiency. The weight of silver actually recovered, divided by 4.025, the weight in grams of silver that should have been deposited in 1 ampere-hour was: $\frac{11.215}{4.025} = 2.79$ ampere-hours, which should have sufficed to precipitate that amount of silver at 100 per cent electrical efficiency.

Therefore a total of 3.378 of the 126 ampere-hours was actually utilized. Hence the total electrical efficiency was: $\frac{3.378}{126}$, or 2.68 per cent. This is a much higher efficiency than that of the Siemens & Halske process, and the capacity, being at the rate of 5 tons per 24 hours in a 1-ton box, is nearly double. The reason for the higher efficiency is that a shorter current gap is used, being only $\frac{1}{2}$ inch, as against $1\frac{1}{2}$ to 3 inches. In the Siemens & Halske process it is not possible to bring the electrodes near one another on account of the danger of short circuits from the loosely hanging lead-foil cathodes. It is probable that in practice I should have had to increase the distance between the electrodes, owing to corrosion of the anodes; but with peroxidized-lead anodes, provided with vertical separators of wooden strips, placed about 6 inches apart horizontally, better precipitation could have been safely obtained with even a $\frac{1}{4}$ -inch current gap.

CRITICISMS OF THE CHRISTY PROCESS.

In 1903 there appeared in Halle a small volume on "Cyanide processes of gold recovery," being one of the "Monographs on applied electrochemistry," edited by Viktor Engelhardt, chief engineer and chief chemist of the Siemens & Halske Co., Vienna. This particular book is written by Manuel von Uslar, with the assistance of Dr. Georg Erlwein,^a engineers of the Siemens & Halske Co., Berlin.

From this combination of electrochemists, representative of Siemens & Halske, much might have been expected, particularly as regards a description of the Siemens & Halske process: but although the process is mentioned, the description is meager and the fund of information that might have been reasonably expected is entirely missing. Concerning my process of "progressive electroconcentration" these authors remark:

Attention need only be called to the great sums that must be invested on the large scale in the form of sheet gold and silver to show that this patent can scarcely lay claim to practical consideration. As regards technical considerations it must be remarked that there are insuperable difficulties in continu-

^a Von Uslar, Manuel, and Erlwein, Georg, Cyanid-Prozesse zur Goldgewinnung: Monograph. angew. Electrochemie, 1903, Halle, Germany, 100 pp.

ously watching the electric current, so that anodes to be stripped of their gold (cathodes from bath 1) shall remain in bath 2 exactly till their gold covering shall be removed, which for a rational operation is quite necessary, as otherwise probable losses of gold, of current, power, and electrode material are unavoidable.

I am ready to admit many defects in the process as it appeared in 1900; these I shall refer to later; but the defects that require consideration are not those mentioned by the distinguished authors. No gold and silver sheets have to be provided except those formed in the ordinary course of the clean-up.

Of the Siemens & Halske process, Von Ustar and Erlwein^a speak as follows:

Every month with electrolytic precipitation likewise the clean-up takes place, which, however, is simpler than with the zinc precipitation. Without interrupting the operation one lifts the single cathodes out of the bath in which a newly charged frame (cathode) is replaced, an operation which requires only a few minutes.

They then go on to describe the drying of the lead sheets, and the fluxing and smelting of the lead cathodes weighing 12 to 20 times the weight of the contained gold and silver, all of which has to be cupelled to recover the 6 to 8 per cent of gold. Anyone who has had any experience with the Siemens & Halske clean-up is well aware of the great danger of loss in handling the cathodes during and after the drying. The monthly clean-up withdraws from circulation the same amount of gold and silver as any other process that requires a monthly clean-up.

With the Christy process, the cathodes, when charged, may be removed for stripping and be replaced by a clean cathode without interruption, as in the Siemens & Halske process. Moreover, with the Christy process, a weekly or even a daily clean-up is possible, so that it is not necessary to keep so much gold and silver in an unproductive state; neither must 12 to 20 pounds of lead be cupelled for each pound of gold, nor must the lead be reduced and rolled into sheets to be again used as cathodes.

As regards the second criticism of these authors, namely, that of a necessity of watching the current to determine exactly when plates are stripped, the criticism is not warranted. If 1 volt or less is used in the clean-up box the plates strip rapidly, do not corrode appreciably, and require practically no attention except removal, washing, and replacing in the deposition box for a new coating. If necessary, an electric bell could be devised to indicate when the plates were sufficiently stripped. When the solution in the clean-up box becomes rich, by raising the voltage the gold and silver are recovered by electrolysis much more easily than from the original solution.

^a Von Ustar, Manuel, and Erlwein, Georg, Cyanid-Prozesse zur Goldgewinnung: Monograph. angew. Electrochemie, 1903, Halle, Germany, 100 pp.

Since writing the above statement I have seen an important paper by Neumann.^a He remarks, "It is true Christy's proposition has some weak points, but certainly it does not fail for the reason given by Von Uslar and Erlwein." Neumann gives the results of some valuable experiments on the efficiency of electrical precipitation under the conditions of the Siemens & Halske process. However, he did not entirely reproduce the conditions, but kept the gold content constant by adding gold to the solution and, instead of keeping a constant voltage as in the Christy process, he maintained a constant current with increasing voltage. He seemingly did not attempt a complete precipitation as is necessary in practice. With a current density of 0.5 ampere per square meter, and with 10 grams of gold present per cubic meter, he found as a maximum efficiency 3.81 per cent; whereas, for the same density of current and with 3 grams of gold present per cubic meter, the efficiency is only 1.33 per cent. With a lower current density he got, for 0.25 ampere per square meter and 10 grams of gold per cubic meter, an efficiency of 7.56 per cent, and for 3 grams of gold per cubic meter, 3.15 per cent. For greater current densities such as 2.4, 4, and 9 amperes per square meter, and with 10 grams of gold present per cubic meter, he found the maximum efficiency to be 0.41, 0.24, and 0.16 per cent. It is evident that if the attempt had been made to reduce the gold content to a minimum the efficiency would have been lower.

Neumann points out what he claims to be the weak points of the Christy electroconcentration process. First, he claims that neither lead nor iron can be used alternately as cathodes and as anodes in cyanide solutions, as those metals are attacked by the cyanide and rendered unfit to serve as cathodes after having served as anodes in the clean-up cell. He fails to observe that the Christy patent states, "The anodes and cathodes may be made of any electroconducting material not too strongly acted on by the solution." Though lead and iron are mentioned, the Christy patent is not confined to their use. I have successfully used Acheson graphite sheets and other forms of carbon. I am ready to acknowledge that there is difficulty in the use of lead. However, the difficulty does not arise from the cause assigned by Neumann, but from local action if the electrodes are not used continuously and are put away damp.

Neumann quotes some experiments, made presumably under his direction, by Mr. John Johnston, in which gold was deposited on carbon cathodes after which an electric clean-up was attempted, supposedly with the Christy process. In the first four experiments,

^a Neumann, B., Electrolytic precipitation of gold from cyanide solutions: *Electrochem. and Met. Ind.*, vol. 4, August, 1906, p. 300.

with a current density of 992 to 118 amperes per square meter, no gold at all was deposited. (Seemingly, the current deposited the gold in the form of slime, which was easily washed off by the violent agitation.) With 24 to 69 amperes per square meter the efficiency, 0.03 to 0.045 per cent, was low, and was higher with the lower density. The voltage, an important item, is not given. The stripping went on easily, but he forgets that the cyanide solution was strong—17.76 to 12.1 per cent. It is remarkable that any gold was precipitated from so strong a solution of free cyanide.

Examination has been made of samples of the silver and gold precipitated by the Christy process, the metal having been first deposited upon iron cathodes from weak solutions, then redissolved by making anodes of these cathodes in a 0.1 to 1 per cent cyanide solution, and reprecipitated upon sheet-iron cathodes, coated with a film of graphite and vaseline. The samples showed that it is possible to deposit coherent sheets of both gold and silver by the Christy process in exactly the way specified in the patent. After wrongly condemning the process as impossible, Neumann proposes to resort to carbon cathodes, which he would strip, causing the gold to be redeposited by the Wohlwill process, sodium chloride, gold chloride, and free hydrochloric acid being used as an electrolyte. By this means good results are obtained with pure gold, and a high efficiency results; however, upon calculating the gold as univalent the efficiency would be modified.

Mention should be made of the fact that the Wohlwill process is not applicable to alloys containing more than 10 per cent silver. With solutions carrying, as many do, more silver and copper than gold it is doubtful whether this ingenious modification of the Christy method would be applicable. The process could not be used to produce fine gold, as Neumann supposes, but by using cyanide, of a proper strength, and employing a proper voltage, the gold and silver could be recovered if the process were properly conducted. The operation is especially easy if cathodes composed of thin sheets of Acheson graphite are used as "cathode anodes." As pure cyanides free from sulphates and chlorides can be used in the stripping box, they are little corroded at the low voltage used in the Christy process.

SUBSEQUENT PATENTED PROCESSES.

C. P. Stewart, U. S. patent 676526, July 16, 1901.—The solution flows over a stationary mercury cathode. The process is similar to the "Molloy process."

William Orr, U. S. patent 689018, December 17, 1901.—Inventor uses zinc anodes in cyanide solutions, especially when the solutions contain copper, and regenerates the cyanide by throwing down the zinc by KIO_4 and Na_2S . The patent resembles one granted to C. H. Merrill for regenerating cyanide from solutions containing zinc.

E. D. Kendall, U. S. patent 698292, April 22, 1902.—The specifications of this process show an electrodeposition box containing carbon anodes in porous cells. The remaining space of the outer vessel is filled with fragments of carbon, which act as cathodes upon which the gold and silver are deposited. After sufficient time the caustic potash is withdrawn from the porous cell and a cyanide solution, adequately strong, supplied to fill it. The carbon plate is then removed and a silver-plated copper plate is made the cathode in place of the anode. The gold and silver dissolve from the first carbon anode and deposit upon the inner plate. The invention contains ideas shown in the Christy patent (No. 643096) previously mentioned, but without the removable cathodes. In one place the inventor specifies a pressure of 5 volts and in another preferably 15 volts. It is evident that the porous cell is a disadvantage, as it increases the resistance enormously. I can not find any place where the process has been applied.

S. Muffly, U. S. patents 714598, 714599, November 25, 1902.—This patent is for a process and an apparatus. A carbon anode is used with a cathode composed of a filiform mass of lead and zinc.

THE BUTTERS PROCESS.

Charles Butters (U. S. patent 756211, Apr. 5, 1904) claims the use of a dense current in combination with peroxide-of-lead anodes and tin-coated steel cathodes. His claims are as follows:

First. The improvement in the process of precipitating metals from solutions, chiefly cyanide solutions, which consists in employing cathodes having surfaces of tin and a high-density electric current, substantially as described.

Second. The improvement in the process of precipitating metals from solutions which consists in employing cathodes having surfaces of tin in combination with anodes of lead peroxide and a high-density electric current, substantially as described.

Third. The improvement in the process of the electrolytic separation of metals from solutions which consists in using a cathode having smooth surfaces of tin, substantially as described.

In the specifications, Butters directs that the anodes and cathodes shall be placed about 3 inches apart, and that the solution containing the metal or metals to be deposited shall be caused to flow between the electrodes, preferably in an upward or downward direction, at a uniform velocity, while an electric current of high density enters the cathode. In practice about 0.5 ampere per square foot of cathode is found suitable, as a rule. The dissolved metals are then deposited in a loose slimy form on the tin cathode surface and may be removed by brushing or wiping the plates with a soft material, such as rubber or wood. This may be conveniently done by removing the cathodes from the solution when the deposit is sufficiently thick, or usually by

running a wiper over the plates at intervals of, say, once a day while in position in the solution, and allowing the removed slime to settle to the bottom of the vessel. This slimy deposit is removed from the vessel at regular periods, and the metals are separated and refined in the usual way.

It may be noted that in the Christy patent, issued in 1900, I disclose the use of a dense current with flat electrodes in the following words: "The current should be so graduated that it (the gold) is deposited in a firm, coherent coat. If a strong current is used, the gold is deposited on a cathode as a fine brown powder, which may be brushed off at intervals and melted down: but I prefer to deposit it as a firm, coherent coat to avoid mechanical loss in handling." Butters's process has been developed on a large scale in several of his plants in this country, Mexico, and Central America, and may be said to be technically successful, but there are at least two practical objections to it. The first is that so high a current density as he employs to separate the material in a loose form on flat electrodes is wasteful. The second is that the recovery of the precipitated slime by removing the plates and wiping them by hand involves much labor, and if the precipitate is scraped from plates and allowed to accumulate at the bottom of the tank there is not only a danger of loss, either by resolution or by mechanical means, but the precipitate is liable to be contaminated by the peroxide of lead that occasionally drops from the anodes to the bottom of the tank, or especially by the precipitated carbonate of lime which is continually settling out of the solution.

That this contamination of the gold is serious I have demonstrated by analyzing a precipitate coming from one of the Mexican plants where the process was used. The precipitate from the head of the boxes contained enough lead and oxide of lead to make it melt almost like butter, but the precipitate from the lower end of the tank contained so much carbonate of calcium that fusing was difficult. The bullion produced from each precipitate was necessarily of low grade. Nevertheless the process is in successful use. It is probably the only electrolytic process now in actual use for the treatment of cyanide solutions from gold and silver recovery.

EFFICIENCY OF BUTTERS PROCESS.

An admirable account of the Butters process is given by Hamilton.⁶ The solution from the sand treatment has the following gold and silver content:

⁶ Hamilton, E. M., A development in electrolytic precipitation of gold and silver from cyanide solutions: *Electrochem. Ind.*, vol. 2, April, 1904, p. 131.

	Gold, pennyweights.	Silver, ounces.
Head solution	2.93	3.51
Tail solution	0.26	0.29
Precipitated per ton solution	^a 2.67	^b 3.22

There were precipitated, at 3 volts, 216 tons of solution a day; hence there was recovered 898.56 grams of gold and 21,632.40 grams of silver. In depositing the gold there was utilized $\frac{898.56}{7.35} = 122.2$ ampere-hours. In depositing the silver there was utilized $\frac{21,632.40}{4.025} = 5,374.5$ ampere-hours, making a total of 5,496.7 ampere-hours. The area of cathodes was 6.950 square feet, with a current density of 0.55 ampere per square foot, or a total of 3,822.5 amperes; and in 24 hours we have 91,740 ampere-hours, or an electrical efficiency of $\frac{5,496.8}{91740}$, which is slightly less than 6 per cent ampere efficiency. There was precipitated 91.1 per cent of gold, and 91.7 per cent of silver.

The solutions from slime treatment had the following content:

	Gold, pennyweights.	Silver, ounces.
Head solution	1.10	1.45
Tail solution	0.13	0.15
Precipitated per ton of solution	.97	1.30
	1.5085	40.4345

There was precipitated, at 2.6 volts, 480 tons of solution per 24 hours, and the recovery was 724.08 grams of gold and 19,408.56 grams of silver. Hence there were utilized in precipitating gold $\frac{724.08}{7.35} = 98.5$ ampere-hours, and in depositing silver $\frac{19,408.56}{4.025} = 4,822$ ampere-hours, making a total in useful work of 4,920.5 ampere-hours. The cathode area (like that of the anodes) was 13,536 square feet. The density of 0.3 ampere per square foot gives a total current of 4,060.8 amperes; or, of 97,459 ampere-hours, only 4,920.5 were utilized, and the electrical efficiency was only 5.05 per cent. The results are much better than those of Siemens & Halske, owing to the use of peroxide of lead instead of rusty iron for the anodes and of bright tin instead of lead for the cathodes. There was precipitated 88.2 per cent of gold and 89.6 per cent of silver. It should be remarked that there was precipitated simultaneously by the current an amount of copper of almost half the weight of the silver. This would considerably increase the electrical efficiency.

Taking the results quoted in Hamilton's figures for November and December, 1901, and for convenience converting ounces to grams by multiplying by 31.1, the figures are:

	Grams.
Total gold deposited in two months	84,872
Total silver deposited in two months	2,204,772
Total copper deposited in two months	1,024,030
For gold, dividing by 7.35, the number of ampere-hours utilized is	11,547
For silver, dividing by 4.025, the number of ampere-hours utilized is	547,769
For copper, dividing by 2.372, the number of ampere-hours utilized is	431,716
Total (supposing copper to be univalent) number of ampere-hours utilized is	991,032

During this time there was actually used 11,013,640 ampere-hours; hence the efficiency was 9 per cent. If, however, as Hamilton assumes, the copper was bivalent 432,000 ampere hours should be added for the copper, making a total of 1,423,032, or an efficiency of 12.9 per cent. Either result is a great improvement on that by the Siemens & Halske process.

In different experiments with various tonnages of these solutions, Hamilton has obtained efficiencies of 4.83, 6.10, 13.24 and 13.90 per cent, but he has not calculated the average. He has used practically the equivalents that I have taken for gold and silver, but for copper a decidedly lower one, being 1.206, as against the 2.372 which I used for univalent copper.^a

It is altogether probable that copper, like gold and silver, is univalent in cyanide solutions; moreover, cupric cyanide is a very unstable compound. Gmelin and Hittorf both claim that copper dissolves only as cuprous cyanide. I have not investigated the subject, but have reason to believe that, at the anode, copper cyanides are formed which are of higher valence than 1, and that these compounds are subsequently reduced to others of lower valence at the cathode. This is one of the reasons that copper cyanide is so hard to precipitate by electrolysis.

STUDY OF CONDITIONS GOVERNING ELECTROLYTIC DEPOSITION.

It must be evident that the results obtained at Bodie were good, so far as precipitation is concerned. However, in 24 hours, with the box used not more than 5 cubic feet of solution could be treated per cubic foot of box capacity. The maximum duty of the deposition box would be at the rate of 5 tons a day for a box holding 1 ton of

^a Standard Handbook for Electrical Engineers, 1915, pp. 1560-1564.

solution. This rate did not seem to me to be satisfactory, yet when I attempted to increase the velocity of the solution above this rate, a poor precipitation resulted.

While I was making these experiments at Bodie, it occurred to me that a good way to increase the capacity of the box would be to circulate the solution by pumping it repeatedly through the box, thus concentrating the gold

and silver upon a smaller number of electrodes than would be necessary if the box were made large for complete precipitation by one passage. I then determined to make a systematic study of all elements necessary to procure complete and rapid precipitation of gold and silver by electrolysis. I had long investigated the effect of the current with sheet-iron electrodes upon a solution of cyanide of potassium at rest.

In referring to this past work I found that there had been used about one-half liter of 1 per cent cyanide solution at rest. Into this solution I immersed a sheet-iron anode $12\frac{1}{2}$ by 13 centimeters in size, and a sheet-lead cathode of about the same dimensions, spacing these $1\frac{1}{4}$ inches apart. I used a storage battery of approximately 2 volts at first, and after $2\frac{1}{4}$ hours raised the voltage to 4 volts. The resulting ampere curves and the cyanide curves are shown in figure 1.

The experiment lasted 45 hours. At the end of the period the cyanide was reduced to 0.03 per cent, showing that 97 per cent had been destroyed. It will be seen that the current diminished almost immediately, owing to polarization effects and oxidation of the

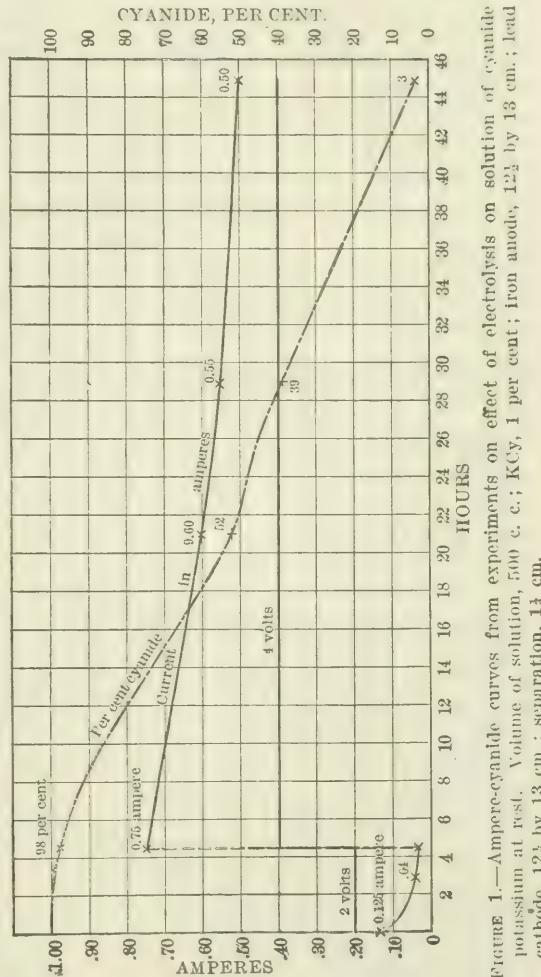


FIGURE 1.—Ampere-cyanide curves from experiments on effect of electrolysis on solution of cyanide potassium at rest. Volume of solution, 500 c. c.; KCY, 1 per cent; iron anode, $12\frac{1}{2}$ by 13 cm.; lead cathode, $12\frac{1}{2}$ by 13 cm.; separation, $1\frac{1}{4}$ cm.

anode. The anode was only slightly oxidized, an almost imperceptible film of oxide of iron having formed.

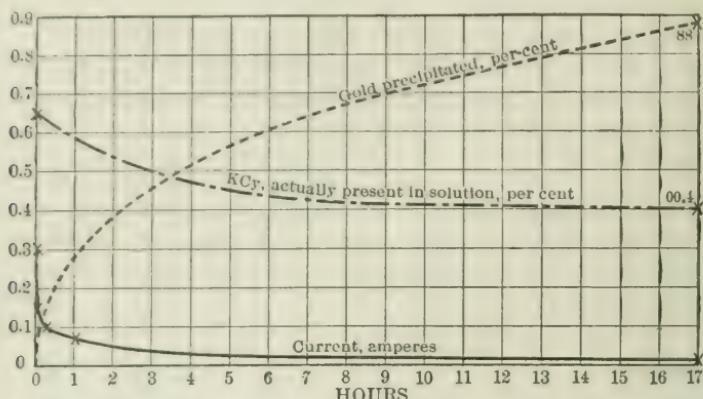


FIGURE 2.—Curves from experiments on electrodeposition of gold from solution of cyanide of potassium. Iron anode, $12\frac{1}{2}$ by 13 cm.; lead cathode, $12\frac{1}{2}$ by 13 cm.; current, 2 volts from storage cell; KCy, 0.065 per cent; Au, 0.005 per cent; volume of solution, 500 c. c.; Au, 2.5 mg. = \$3 a ton; electrodes 14 cm. apart.

Following these tests and in the same apparatus a cyanide solution was treated containing 0.065 per cent of free cyanide and \$3 a

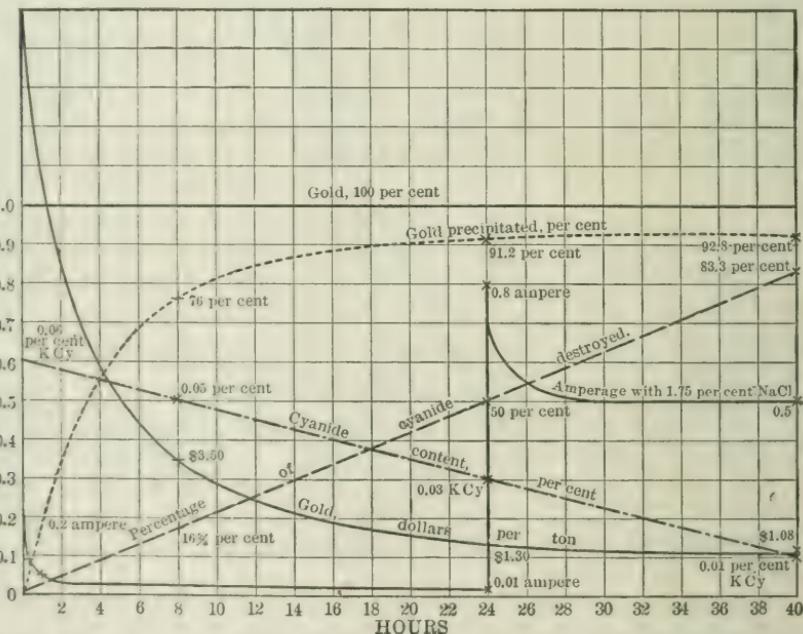


FIGURE 3.—Curves from experiments on electrodeposition of gold from solution of cyanide of potassium. Iron anode, $12\frac{1}{2}$ by 13 cm.; lead cathode, $12\frac{1}{2}$ by 13 cm.; electrodes 14 cm. apart; current, 2 volts from storage cell; volume of solution, 500 c. c.; Au, \$15 a ton; KCy, 0.065 per cent.

ton in gold. The results of the experiment showed that in 17 hours only 88 per cent of the gold was precipitated. The cyanide was con-

tinuously destroyed, only 0.04 per cent remaining at the end of the experiment. The results of this test are shown in figure 2.

In the same apparatus a 0.06 per cent cyanide solution containing \$15 a ton in gold was treated. One storage cell was used and the experiment lasted for 40 hours. The results are shown in figure 3.

At the end of 24 hours the gold was reduced from \$15 to \$1.30 a ton. One-half the cyanide then had been destroyed. At this time I added sodium chloride, a suggestion of Mr. Butters, so as to make a solution containing 1.75 per cent NaCl. The current jumped immediately from about 1 milliampere to 800, and at the end of 40 hours remained 100 milliamperes. The gold had been

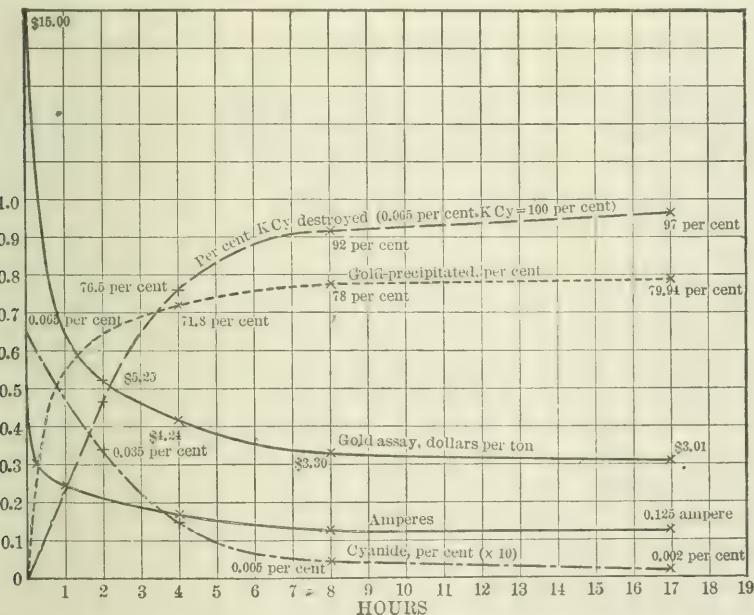


FIGURE 4.—Curves from experiments on electrodeposition of gold from solution of cyanide of potassium. Iron anode, $12\frac{1}{2}$ by 13 cm.; lead cathode, $12\frac{1}{2}$ by 13 cm.; electrodes $1\frac{1}{4}$ cm. apart; current, 4 volts from two storage cells; Au, \$15 per ton; KCy, 0.065 per cent.

reduced to \$1.08 a ton, and the cyanide to 0.01 per cent, so that only 83.3 per cent of the gold was precipitated. Five-sixths of the cyanide had been destroyed. The low rate of precipitation in this experiment led me to increase the voltage to 4 volts, using two storage battery cells. For this I used an 0.065 per cent cyanide solution containing gold to the value of \$15 a ton, the remaining conditions being as before. The results are shown in figure 4. At the end of 17 hours the cyanide had been reduced to 0.002 per cent, 79.94 per cent of the gold had been precipitated, and 97 per cent of the cyanide had been destroyed. The results did not then look promis-

ing, but when compared with the results of my later experiments, they show the great progress that has been made in this investigation.

One of the first things to be noted in the results is the rapid fall of the current, which continued to decrease throughout the whole process. I noticed that whenever either of the electrodes was agitated so as to displace the solution in immediate contact, the current immediately increased, falling again as soon as the solution came to rest and the conditions were reestablished by electrolysis. This was evidently due to the well-known phenomena of polarization. It was made evident by these experiments that the precipitation of gold and silver from cyanide solutions was a problem of great difficulties.

HOW DOUBLE CYANIDES REACT IN ELECTROLYSIS.

The solutions of the double cyanides seemingly act much differently from those, for instance, of either sulphates or chlorides of a metal like copper. With solutions of these latter salts rapid and complete precipitation would at once ensue. To those familiar with the conditions of electroplating gold and silver in cyanide solutions, the electrodeposition process seems to be a natural and easy one; but the conditions there maintained are different from those prevailing in solutions used in ore treatment. With solutions such as are used in electroplating the density is sufficient to produce a very good conductor. The solution is rich in gold or silver, and the metal deposited is replaced as fast as it is precipitated by a supply from the soluble anodes. Hence the electrochemical conditions are suitably maintained. However, in the treatment of solutions resulting from ore treatment, solutions have to be handled that assay less than \$6 per ton, and contain less than 0.001 per cent of metallic gold. This solution must, perhaps, be reduced to less than 6 cents per ton, or 0.00001 per cent of gold. No one would attempt such a task with a metal less valuable than gold or silver.

The first part of the gold in electrolysis is readily removed, but the deposition becomes increasingly difficult toward the end, and it is theoretically and practically impossible to remove the last traces of the gold from such solutions. The chief cause of the great difficulty is that the gold and silver form what are known as "complex ions" in the cyanide solution. For instance, if a solution containing pure KAuCy_2 but no free cyanide be considered, one is dealing with a substance which crystallizes in white crystals, looking very much like granulated sugar, soluble in water and forming a colorless solution. This solution, if sufficiently dilute, according to the ionic theory breaks up into two ions, the simple ion K carrying a positive charge of electricity, and the complex ion AuCy_2 carrying a negative

charge. When an electric current is passed through such a solution, with platinum electrodes, the potassium ion carrying the plus charge of electricity travels to the negative pole, and if there is sufficient gold cyanide in the vicinity it decomposes some of the cyanide, precipitating the gold on the cathode and setting free the cyanide. Meantime the complex ion AuCy_2 , with its negative charge of electricity, travels to the anode, and there forms a pale yellowish, slimy film which protects the anode from further action by the current. Hence, with such a solution, electrolysis soon comes to a stop, the anode being insulated by the slimy coat of AuCy_2 .^a As was proved by Hittorf,^b the same action takes place with potassium argento-cyanide, the only outward difference being that the slimy film of AgCy_2 is white.

Because of the formation of the insoluble and insulating slimes on the anode it is always necessary, in electroplating, to have some free cyanide of potassium in the solution to redissolve this film. Caustic potash may be used instead, but is not so satisfactory. For instance, AuCy_2 partly decomposes into AuCy and Cy . The Cy partly oxidizes to cyanate and partly changes to cyanide of potassium. AuCy redissolves in the excess of free cyanide if present, or in KHO if only the latter is present. With the KHO , cyanate and cyanide of potassium are formed and the essential salt of the solution is regenerated. This rather complicated process is hard to understand and a little difficult to explain, but there is no doubt about its occurrence. As regards silver cyanide the reactions mentioned were demonstrated quantitatively by Hittorf.

In order to appreciate the importance of this peculiarity of cyanide solutions, consideration might be given to the electrolysis of nitrate of silver. The Ag goes directly to the cathode, and NO_3 travels to the anode. Hence for every atom of silver precipitated at the cathode one atom disappears from the solution near the cathode. But in the electrolysis of cyanide of gold or silver, for every atom of gold or silver precipitated at the cathode two atoms are removed by the current, one being precipitated by the K ion and the other traveling to the anode. Hence it must be evident that the action of the current renders further precipitation of the gold more and more difficult. Julian and Smart^c claim that this discovery was made by Daniell and Miller. They say—

Daniell and Miller (Philos. Trans., 1844, p. 1) investigated the nature of the ions, and found that when an electric current is passed through a solution of KAuCy_2 or KAgCy_2 the K is the positive ion and goes to the cathode, while

^a See Christy, S. B., On the solution and precipitation of cyanide of gold: Trans. Am. Inst. Min. Eng., vol. 26, 1896, p. 758.

^b Hittorf, W., Über die Wanderungen der Ionen während der Elektrolyse, 1859; reprinted in Ostwald's Klassiker der exakten Wissenschaften No. 23, 1891, p. 74.

^c Julian, H. F., and Smart, Edgar, Cyaniding gold and silver ores, 1904, p. 121.

the negative ion consists of gold or silver and cyanogen, and this goes to the anode. Hittorf has since confirmed this and assumes the negative ion to be AuCy_2 for gold and AgCy_2 for silver. That is to say, that when these complex salts are electrolyzed, the gold and silver move in the opposite direction to that taken in the case of simple salts.

The foregoing abstract quotation appears to contain several misstatements: In the first place, nowhere in the reference given do Daniell and Miller make any reference to the cyanides of gold or silver. They do discuss potassium ferro and ferri cyanide, cyanide of potassium, and sulphocyanide of potassium, but nowhere in the article mentioned nor in any other of the *Philosophical Transactions* from 1842 up to 1860, do they make any statement that can be twisted into such an assertion. They state that they intend to investigate other cyanides, but they do not seem to have done so.

It may further be remarked that the work of Hittorf seems to have been both underrated and overrated. No references by Julian and Smart are given to Hittorf's^a work, a full account of which has been reprinted by Ostwald. The work of Daniell and Miller was of great importance to electrolytic science, but it contained numerous errors which were cleared up by the skillful work of Hittorf which is a model of scientific accuracy. Hittorf with punctilious care seems to have given full credit to Daniell and Miller for the good work done by them, but there is no mention of their having done any work with the cyanides of gold and silver. He seems to have been the first to have shown that in the electrolysis of a KAgCy_2 solution the K goes to the cathode and the AgCy_2 to the anode. However, he makes no mention of KAuCy_2 solution, though he does treat of HAuCl_4 .

Ostwald^b has collected data on all the known velocities of ionic transfer, and he gives the values for K and $\text{Ag}(\text{CN})_2$ and credits the work to Hittorf. Nowhere is any mention made of K and AuCy_2 , though the list covers eight pages. Hence I assume that Julian and Smart have claimed too much for Daniell and Miller. Whether I was the first to call attention to the nature of the electrolytic reaction in solutions of KAuCy_2 ,^c I do not know; but I believe that I can fairly claim to have been the first to bring out the practical importance of it in electrodeposition from cyanide solutions. The reaction is of controlling importance in all electrocyanide processes and yet it is not understood by many of the writers on the cyanide process or by many authors of chemical textbooks.

^a Hittorf, W., *Über die Wanderungen der Ionen während der Elektrolyse*, 1859; reprinted in Ostwald's *Klassiker der exakten Wissenschaften* Nos. 21 and 23, 1891, 87 and 142 pp.

^b Ostwald, Wilhelm, *Chemische Enérgie*, 2d ed., 1893, p. 608.

^c See Christy, S. B., *The solution and precipitation of cyanide of gold*: *Trans. Am. Inst. Min. Eng.*, vol. 26, 1895, pp. 758-759.

Sir Humphrey Davy's original idea as to the composition of salts as against the ideas of his time has been confirmed by more recent scientific investigations. Daniell and Miller do not seem even to have been the first to discover the complex ions of potassium ferrocyanide, ferri-cyanide, and sulpho-cyanide. To Hittorf belongs the credit of expanding and completing the application of the results of early investigators to potassium silver cyanide. Ostwald deserves the credit of generally clearing up the subject by the invention of the term "complex ion." As far as I am aware he did not extend his work to include KAuCy_2 .

The separate experiments upon which I based the statements made in 1896 were with cyanides of silver, of gold, and of copper. I used pure solutions of the double salts of potassium and of the several metals without free cyanide. A platinum dish was the cathode, a platinum wire the anode. I found that the current was soon stopped by the formation of a nonconducting slimy coating of varied color. With KAgCy_2 the coating was of a pale white appearance and had a faint yellow cast. The slime from the KAuCy_2 was yellow with a pale green cast. With copper the anode slime was a bright grass green or yellowish green. The accumulation of any one of these precipitates gradually stopped the electric current. When the crust of precipitate was scraped off the anode, so as to fall on the cathode, it retained its shape but was reduced to the metal—silver, gold, or copper—according with the composition of the double cyanide. Similar crusts form on the anodes in electroplating when insufficient free cyanide is used, as is well known to all electroplaters, but I have not been able to find the explanation of this phenomenon in any of the many books on electroplating published before 1896.

Fortunately a comprehensive bibliography on this subject has been prepared by McBain.^a It is claimed to be complete to the end of the year 1905. All the work of Daniell is included in this outline, and no mention is made of his ever having determined the migration velocities of KAgCy_2 or of KAuCy_2 . The relative velocity of the potassium ion in KAgCy_2 was determined to be 0.594 in a solution containing 1 gram-molecule in $1\frac{1}{2}$ liters.^b Nobody seems to have determined the migration velocities of the ions of KAuCy_2 up to the end of 1905.

Unfortunately at variance with the statements made by Julian and Smart, the fact appears that Daniell was not the first to observe the true nature of electrolysis of complex ions.

^a McBain, J. W., Experimental data of the quantitative measurements of electrolytic migrations: Wash. Acad. Sci., vol. 9, July 31, 1907, pp. 1-78.

^b Hittorf, W., Über die Wanderungen der Ionen während der Electrolyse, 1859; reprinted in Ostwald's Klassiker der exakten Wissenschaften No. 23, 1891, 142 pp.

The first observer seems to have been Robert Porrett in 1814.^a The paper mentioned is signed "Tower, June 6, 1814." It would appear from the large number of French chemical terms used that Mr. Porrett must have been a Frenchman, probably residing in England, and not a member of the Royal Society.

Porrett seems to have had a correct idea of the composition of the salts known as triple prussiates, and to have fought the idea then prevailing that the triple prussiates were simple, double cyanides. Thus, he says:

I consider the salts termed triple prussiates as binary compounds of an acid with a single base; as salts which do not contain any prussic acid, nor any oxide of iron as a base, although both the substances may be obtained from them by a decomposition of their acid.

The first experiment which I shall adduce in support of the above opinion is one with the voltaic battery; it appeared to me that this instrument would show whether the oxide of iron in the triple prussiates existed in them as a base, or as an element of a peculiar acid by attracting it to the negative pole in the former, and to the positive pole in the latter case. I therefore exposed a solution of triple prussiate of soda to the agency of a small battery of 50 pairs of double plates of one inch and a quarter square, kept in action for 20 hours, the solution was connected by platinum wire with the negative pole, and by filaments of cotton with distilled water which communicated by platinum wire with the positive pole. Thus circumstanced the triple prussiate of soda was decomposed, its acid (consisting of the elements of prussic acid and black oxide of iron) was carried over to the positive pole; here meeting with oxygen from the decomposing water, it underwent a farther change by which it was converted into prussic acid which was partly volatilized, and into blue triple prussiate of iron which formed there in abundance; the liquid at the negative pole after this process contained only soda with a trace of undecomposed triple prussiate. In this experiment I consider the circumstance of the black oxide of iron being carried over to the positive pole as a proof that it went there as an element of an acid, for as a base it must have remained at the negative pole.

Porrett seems to have discovered also sulpho cyanate of potassium (which he calls "red-tinging acid") by boiling Prussian blue with sulphide of potassium, and also by heating to redness animal charcoal and sulphide of potassium, as well as by other means. He subjected this solution to the action of electrolysis and found that the new acid was carried to the positive pole without decomposition or the separation of any sulphur. This would clearly prove, it seems to me, that to Porrett belongs the credit of first proving the reaction that takes place when "complex ions," as they are now termed, are electrolyzed.

The first quantitative work on "transfer values" seems to have been done with sulphate of sodium by Faraday^b in 1833. Daniell's

^a Porrett, Robert, Jr., On the nature of the salts termed triple prussiates, and on acids formed by the union of certain bodies with the elements of the prussic acid: Phil. Trans. Roy. Soc. Lond., 1814, pp. 527-556.

^b Faraday, Michael, Experimental researches in electricity: Phil. Trans. Roy. Soc. Lond., 1833, pt. 1, p. 86.

first work was reported in 1839, and his last work seems to have been done in 1844, whereas Hittorf's work was from 1853 to 1859.

The theories foreshadowed by Sir Humphrey Davy, proved to be true by Porrett and by Faraday, afterwards confirmed by Daniell and Miller, and carried to perfection in Hittorf's classic work, have been of the greatest importance not only to chemical science but to practical technology. The work of these men, not even yet fully appreciated, was for many years a subject of bitter controversy.

PRACTICAL APPLICATION OF THE LAW.

It soon became evident to me that the necessary electrolytic reaction with the double cyanides was one of the chief causes of slow precipitation, in short, that the gold content at the cathode was so rapidly diminished that the potassium ion when brought to the cathode by the electric current found there no gold to precipitate. Consequently, electrical energy was wasted, water being decomposed, and caustic potash and hydrogen were formed to no useful purpose. The gold was accumulated at the anode where it acted injuriously by increasing the resistance.

It occurred to me that both these evils could be at once met by a rapid circulation of the solution from anode to cathode, so that the gold collected at the anode, where it was doing only harm, could be swept to the cathode where the potassium ions, instead of decomposing water, would precipitate gold. With sheet electrodes it was not easy to obtain this result, whether, as in my first process, the electrodes were transverse to the box, and the circulation up and down between them, or whether, as in most recent installations of the Siemens and the Butters processes, the electrodes hung longitudinally in the box, and the solution passed directly between them. With none of these arrangements could the direct replenishment of the cathode solution, so necessary to good results, be effected. This requirement could be met only by the use of pervious anodes and cathodes, either of sheet metal or of wire cloth. Perforated sheet electrodes were first used but the cyanide of gold and silver accumulated on the anode spaces, between the holes, where the circulation was poor. I then resorted to the use of iron-wire cloth.

The first anodes were made of iron-wire cloth of 8 meshes to the linear inch, the wires being 1 mm. thick. A single sheet was used which was $3\frac{1}{4}$ inches wide by 4 inches high, only about $2\frac{1}{2}$ inches being submerged. It was stiffened by a thin, sheet-iron fold having a copper conductor riveted to the top. The first cathodes were of similar dimensions and were made of one-fourth-millimeter iron-wire cloth of 30 meshes to the linear inch. I afterwards found that such cathodes offered too much resistance to the current and finally made them of about one-half-millimeter wire cloth of 16 openings to the linear inch. Such a piece of wire cloth has almost exactly the

same area for the submerged wires as would be presented by a solid sheet of metal of the same cross section exposed on both sides.

It is well known that when oxidation is desired in electrolysis a large anode area should be used. When reduction is wanted a large cathode area should be used. As reduction rather than oxidation was the purpose of the process it seemed wise to have a larger area of cathode than of anode. Hence, five such cathode sheets were fastened together and brought into contact with a copper conductor, above the water level, by crimping them at the top by a fold of sheet iron and at the bottom by similar small sheet-iron crimps. This makes what I term herein "bunches of five." After various trials I found that two such "bunches of five" cathodes, ten sheets in all, could be effectively inserted between each pair of anodes. The metal then deposits on all of the ten, most of course on the sheets next to the anodes, but upon all in time. These cathodes were three-sixteenths inch thick at the crimps and one-quarter inch at the widest part. The anodes were insulated from the cathodes by vertical rubber bands one-eighth inch thick. This arrangement was compact, giving over five times as much cathode as anode area. Since wire cloth, as manufactured, is coated with a protective coating of oil, it was always necessary to burn this off at a red heat before constructing the electrodes. To avoid undue oxidation, this burning must be done with care, particularly when the wire cloth is to be used for cathodes. A slight film of black magnetic oxide on the anodes is an advantage rather than a detriment, as it partly protects them from attack by the solution. With solutions free from salt and soluble sulphates the iron anodes are hardly attacked. Some of these anodes and cathodes that have been in use at intervals for 14 years are still serviceable.

Another advantage of the wire-cloth cathodes is that a dense current can be used without forming a loose deposit, and hence a rapid deposition can be obtained. The deposited metal tends to form about the wire a tube, which adheres firmly. This has long been recognized in the electrolytic assay of copper, where the use of platinum-wire gauze has so much reduced the time necessary for complete precipitation.

The advantages of the use of wire-cloth cathodes were as follows:

1. Direct and effective circulation of the solution from anode to cathode.

2. Larger area of cathode than of anode.

3. Use of a denser electric current without waste.

All of these advantages were not appreciated at once, but became gradually of more apparent importance as the investigation went on. The first experiments were tentative, and though the methods used were rather crude, compared with later ones, I give them rather fully because of the importance of the details.

PRELIMINARY EXPERIMENTS.

On September 17, 1900, I took a box $28\frac{1}{2}$ centimeters long by 6 centimeters deep and 7 centimeters wide, and holding 1.195 liters (0.0422 cubic foot) of liquid. In this were placed eight anodes made of sheets of 8-mesh iron-wire cloth, of wires 1 mm. in diameter. The nine cathodes were made of iron-wire cloth of 30 meshes to the linear inch. The immersed area of the cathodes was $6\frac{1}{2}$ square inches, or 0.0476 square foot. The actual surface of the cathodes was approximately double that area, or $13\frac{1}{2}$ square inches (0.0952 square foot). I used 8 liters of solution of 0.2 per cent KCy, assaying 15.87 mg. of silver per 100 c. c.

At 3.40 p. m. the first experiment was started, the current being 0.20 ampere, at 1.1 volts, and the solution containing 0.19 per cent KCy and 15.87 mg. of silver per 100 c. c. The source of current was a storage battery of 2 volts on an open circuit. Some resistance was used in series with the battery to adjust the voltage. At 5 p. m. the solution had passed through the box once, and the current was found to be 0.16 ampere at 1.25 volts, the solution containing 0.18 per cent KCy and 5.61 mg. of silver per 100 c. c. The recovery in the one passage through the box was therefore 64.50 per cent.

During this experiment no evolution of gas at the cathodes was visible or audible. After the first run had been finished, 8.4 c. c. of nitrate of silver, or 0.084 gram of silver, got into the solution by accident. In order to neutralize this, a proper proportion of cyanide of potassium was added to the solution. This increased the original assay value of the solution to 16.98 mg. of Ag per 100 c. c. The solution was then left at rest over night, with the battery connected. The voltage rose to 1.75, and the current fell to 0.06 ampere, and by morning the content of Ag had been reduced to 0.30 mg. per 100 c. c.

At 9.25 a. m. the solution was started a second time through the box. The voltage was 1.75 volts and the current 0.10 ampere. The solution had all passed through at 1.30 p. m. The silver had been reduced to 0.74 mg. per 100 c. c., showing that there had been precipitated, in the first and second run, 95.64 per cent of the original content.

At 2.10 p. m. the third run was begun at 1.75 volts and 0.2 ampere. The run was finished at 2.50 p. m. The solution contained 0.16 per cent KCy and 0.54 mg. of silver per 100 c. c. The recovery was 96.82 per cent.

At 2.55 p. m. the fourth run was started at 1.8 volts and 0.35 ampere. The solution contained 0.16 per cent KCy and 0.29 mg. of silver per 100 c. c. The recovery was 98.29 per cent.

At 3.18 p. m. the fifth run was started and was finished at 3.35 p. m. The solution contained 0.16 per cent KCy and 0.20 mg. of silver per 100 c. c. The recovery was 98.82 per cent.

At 3.39 p. m. the sixth run was started and was finished at 5.14 p. m. The solution contained 0.15 per cent KCy and 0.09 mg. of silver per 100 c. c. The recovery was 99.47 per cent.

A résumé of the results during the total period of 8.3 hours follows:

Results of early experiments with electrodeposition of silver.

Run No.	Duration of run.	Recovery.	Silver remaining in residue.
1.....	Hours. 1.55	Per cent. 64.50	Per cent. 35.50
2.....	4.08	95.64	4.36
3.....	.66	96.82	3.18
4.....	.40	98.29	1.71
5.....	.28	98.82	1.18
6.....	1.55	99.47	.53

Some solution was consumed in the samples, but, making no allowance for this, 8 liters of solution was treated, the silver content being reduced to 0.53 per cent in 8.30 hours. The box held 1.2 liters of solution, but the electrodes occupied somewhat less than 1 liter of this space, so that the solution was treated at the rate of about 1 liter per hour in a 1-liter box, the silver recovery being 99.47 per cent. Thus the capacity of the box, with wire-cloth electrodes, was 24 liters per 24 hours, or nearly five times the capacity with the plain electrodes used in my experiments at Bodie. The solution of 8 liters passed through the box six times in the 8.3 hours, or roughly speaking, it required 1.4 hours for 8 liters to pass once, and hence it required on an average 1.75 hours for 1 liter to pass through the box. The average rate of flow through the box was 5.7 liters per hour.

CIRCULATION OF SOLUTION.

The importance of a proper rate of flow through the box is evident from the following notes taken during the first run:

12.30 p. m.—Volts, 1.60; amperes, 0.120; solution in circulation.

12.45 p. m.—Circulation stopped; voltage at once raised to 1.73; amperes fell to 0.070.

1.00 p. m.—Volts, 1.74; amperes, 0.068; solution at rest.

1.30 p. m.—Volts, 1.75; amperes, 0.060; solution at rest.

2.10 p. m.—Solution started through the box for the third time; volts, 1.75; amperes, 0.200.

In all the experiments, when the circulation of the solution was stopped, the current dropped, and the voltage rose. The solution was made to circulate by hand, and after having passed through the box once it was placed again at the head and allowed to flow again, the rate being regulated by the stopcock. The results from the first run indicated that I was on the right track to increase the capacity of

the box, and the subsequent experiments were undertaken to determine the best conditions.

In all my first experiments the circulation was made by hand, as described; but it soon became evident that a rapid rate of circulation was so important that some automatic means ought to be used. For the purpose a small crude centrifugal pump like that shown in figure 5 was made.

A number of persons have tried to verify my results on a small scale without using a proper means of circulation. Centrifugal pumps as small as that shown are not to be purchased and it is

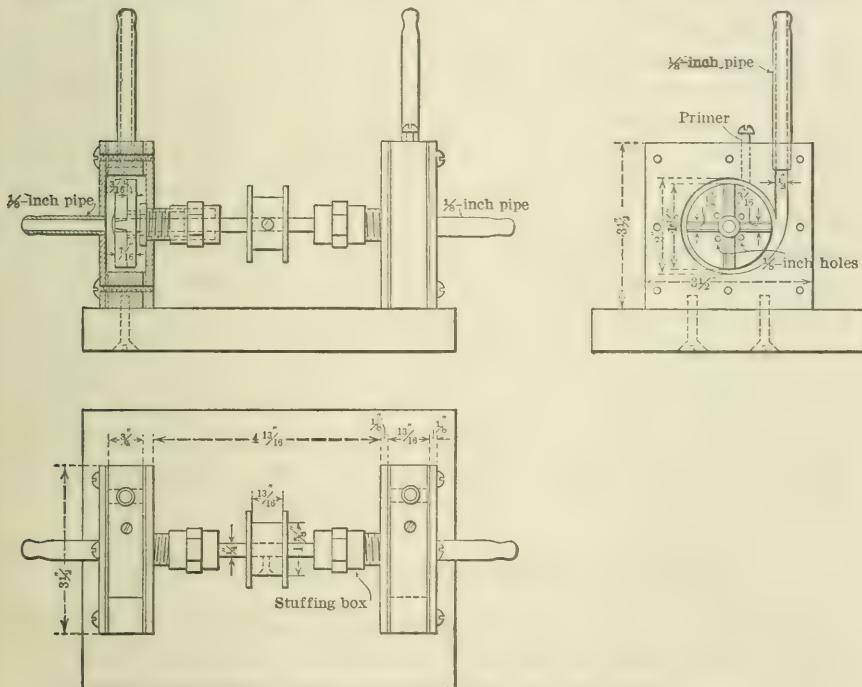


FIGURE 5.—Small double centrifugal pump used in circulating solutions.

necessary to make them, but they need not be elaborate or costly. The small double centrifugal pump shown can easily be constructed in any machine shop at small expense. It gives ample circulation for electrodes 10 by 10 cm., or 4 by 4 inches. This size is most convenient, as it has a sectional area of one one-hundredth square meter or one-ninth square foot, and results can be converted into square meters by multiplying by 100 or into square feet by multiplying by 9.

Two pumps are easier to use than one because they run in better balance (see fig. 5). The pumps rest in a planed base of cast iron 1

inch thick. The body of the pump is a square block of cast iron three-fourths inch thick, planed true and faced on each side with graphited rubber gaskets. In the center of this plate a 2-inch hole is provided. The sides are of thin plates of iron, the outside ones carrying a one-eighth-inch suction pipe having the end turned for a hard-rubber hose attachment. The inner side carries a bearing, with stuffing box. The whole is secured to the inner plate by a lock nut. The packing is well lubricated with a mixture of vaseline and graphite, and should be adjustable to prevent leakage. It is important that the shaft through the stuffing box should be perfectly smooth so as not to cut out the packing. A pulley of thirteen-sixteenths-inch face, slightly crowning, and of 1 $\frac{1}{2}$ -inch diameter, is driven by a small electric motor or a Pelton water wheel. The runner is constructed with four blades and commonly should be placed in a position to be slightly eccentric, and tangent only near the discharge. The position of tangency most desired is not indicated in the particular pump here shown. The clearance elsewhere should be slight. It is important, too, to drill at least four one-eighth-inch holes through the web of the runner to allow it to run in balance. A one-fourth-inch drill hole leads the discharge to a one-eighth-inch pipe with a hose connection at the end.

It is astonishing how important a small pump of this kind is. Hand circulation is impracticable. Air lifts produce an aerated solution that tends to dissolve the gold. The pump shown, easily and cheaply made, has sufficed for thousands of experiments and is still in good order. Of course, for work on a large scale, a well-designed centrifugal pump would be necessary.

EFFECTS OF INCREASING THE RATE OF FLOW.

Most of the following experiments were conducted with solutions of pure silver potassium cyanide (KAgCy_2), which was cheap and convenient. The solutions were highly concentrated and were afterwards diluted to form the free cyanide solution desired, to which also other pure chemicals such as KHO , or CaH_2O_2 , and KCy were added as necessary. When proper precipitation had been procured the silver content was again raised by adding the proper volume of the strong solution, after which the process was continued. Only in this way could the many variable factors be kept under control. By the use of the rigid electrodes and of proper insulating spaces the anodes and cathodes could be brought within one-eighth inch of one another with perfect safety. A more compact construction is well nigh impossible.

At first I gradually increased the rate of flow and found that the capacity of the box increased proportionally. The rate was first

increased to 8 liters per hour, being subsequently increased to 10, 30, 60, and finally 120 liters per hour. The space occupied by the electrodes was about 1 liter. Also it was found convenient to increase the volume of the solution to about 22 liters. The results of a number of tests follow:

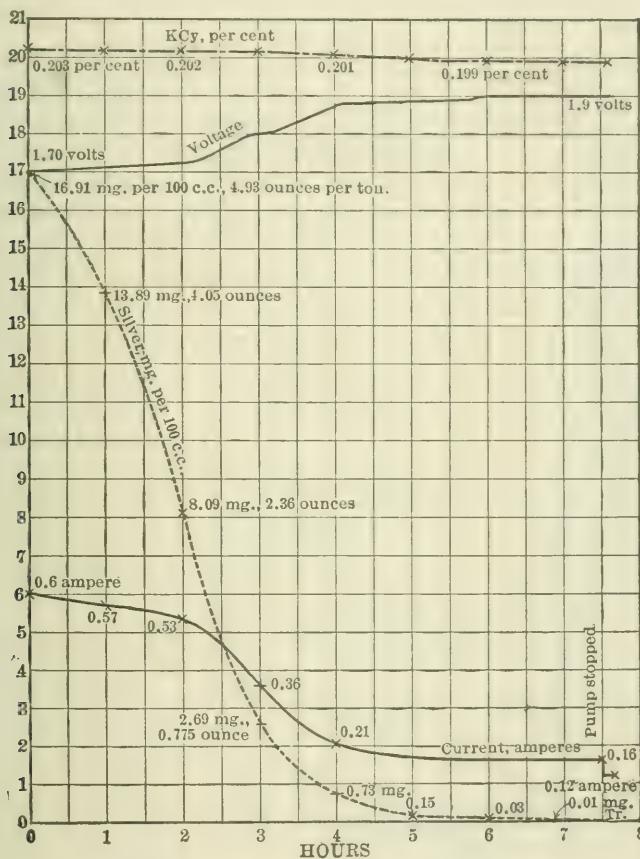


FIGURE 6.—Electrodeposition results with silver cyanide solution with rate of flow of 60 liters per hour; velocity, 9.4 inches per minute through open box, 21 inches through cathodes; 22 cathodes of 30-mesh iron wire, each $2\frac{1}{4}$ by $2\frac{7}{8}$ inches; area, 6.469 square inches; actual wire surface, 1 cathode, 0.1147 square foot, 22, 2.5234 square feet; estimated effective surface, 1 cathode, 0.1 square foot, 22, 2.2 square feet; 8 anodes of 8-mesh iron wire.

On October 5, 1900, I made an experiment with 22 sheet cathodes of 30-mesh wire cloth, and 8 anodes of 8-mesh wire cloth. The cathodes were $2\frac{1}{4}$ by $2\frac{7}{8}$ inches in size. The volume of the solution treated was 22 liters. The rate of flow was 60 liters per hour; the velocity of flow was 9.4 inches through the open box and 21 inches per minute through the cathodes. The estimated effective surface of one cathode was approximately 0.1 square foot, so that 22 cathodes

gave an effective surface of 2.2 square feet, and the actual surface of the wires was 2.52 square feet. The results of this experiment are shown in figure 6.

It will be noticed that there is a slow but continuous decrease in the value of the cyanide solution. The assay value of the silver begins at 16.91 mg. per 100 c. c., or 4.93 ounces per ton. The voltage is between 1.7 and 1.9 volts. Attention is called to the silver precipitation curve. The fall of the silver is very rapid during the first three hours, during the next two hours it becomes slower, and after five hours it appears as an asymptote to the x axis, when the current is seen to be not economically used.

The effect of the increased rates of flow is shown in figure 7.

In the experiment here represented the rate of flow was increased to 120 liters per hour (velocity, 42 inches per minute through cathodes), or double that employed in obtaining the results shown in figure 6; other conditions were the same as in figure 6. It will be noticed that the silver was much more rapidly precipitated than in the previous

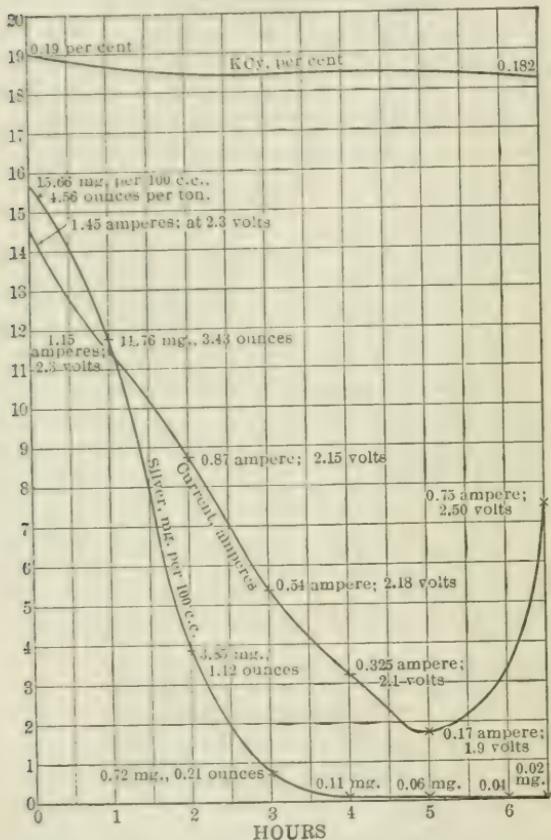


FIGURE 7.—Electrodeposition results with silver solution with rate of flow of 120 liters per hour; velocity, about 19 inches per minute through open box, $4\frac{1}{2}$ inches through cathodes; anodes and cathodes same as in figure 6. Voltage varied.

experiment. The voltage in this experiment varied between 2.1 and 2.5 volts. In spite of the high current density, there was no gas visible on either cathodes or anodes, so long as the solution was in circulation.

Figure 8 shows the results of an experiment similar to that represented in figure 7, except that the area of cathodes was increased. Twenty-two old cathodes of 30-mesh iron wire and two new cathodes, each consisting of 10 sheets of 1-mm. wire cloth, were used. The effec-

tive surface area of the cathodes was approximately 4.2 square feet, or twice that of the cathodes used for the previous test. In this experiment the voltage was controlled better than before. In the beginning 2.03 volts was employed, but after two and one-quarter hours the potential was raised to 2.5 volts, remaining thus until five and one-quarter hours had passed. At the end of the five and one-quarter hours a new charge of KAgCy_2 was added, bringing the total volume again to 21.65 liters and replacing the solution used in the samples. It will be noticed that the current immediately rose from 0.6 ampere, which had been maintained by the 2.5 volts, to 1.45 amperes, and that the voltage fell to 2.35, showing that the solution had become a better conductor. It will also be noticed that the precipitation of silver was much better after a new charge had been added than before. Two hours after the silver solution had been reduced from 17.38 mg. per 100 c. c. to 0.13 mg., or 0.038 ounce per ton. As stated above, the area of cathodes exposed was twice the area of the cathodes shown in figure 6. The precipitation capacity of the box had increased enormously. It was possible to make a new precipitation after adding a new charge of silver at the end of two hours.

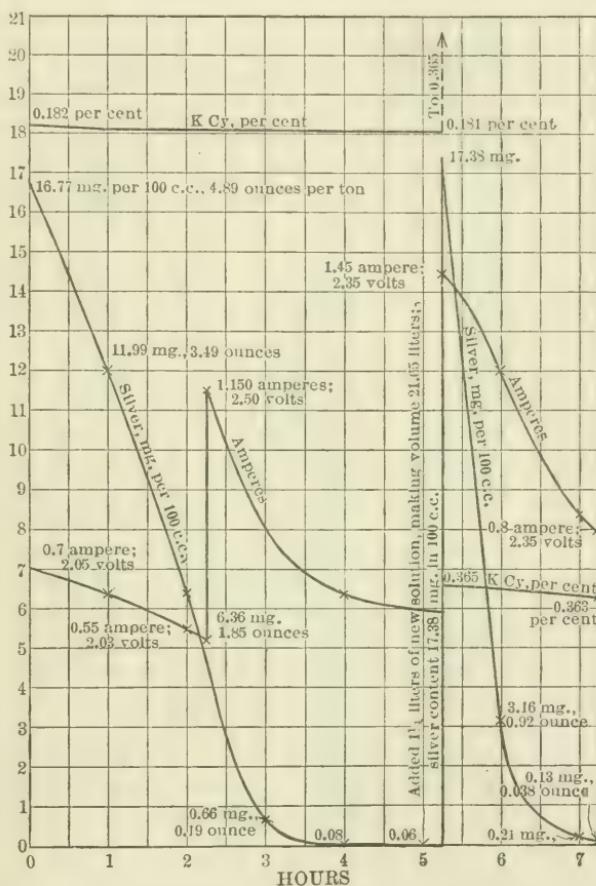


FIGURE 8.—Electrodeposition results with silver solution with rate of flow of 120 liters per hour and larger cathode area. Velocity of flow, 19 inches per minute through open box, 42 inches through cathodes; 22 used cathodes of 30-mesh wire cloth and 2 new cathodes, each of 10 sheets of 1-mm. wire cloth; actual wire surface of one cathode, — sq. cm.; estimated effective surface of 42 cathodes, 4.2 square feet.

Figure 9 shows the results of an attempt to increase the flow of solution to 180 liters per hour. The whole of the solution passed through the box nearly nine times in one hour, and as the box held about a liter, an amount equal to 180 times the volume of the box passed through in each hour. Forty wire-cloth cathodes and seven wire-cloth anodes were used in this experiment. The cathodes were 3.5 by 2.6 inches square and had a total surface area of 6.38 square feet. It

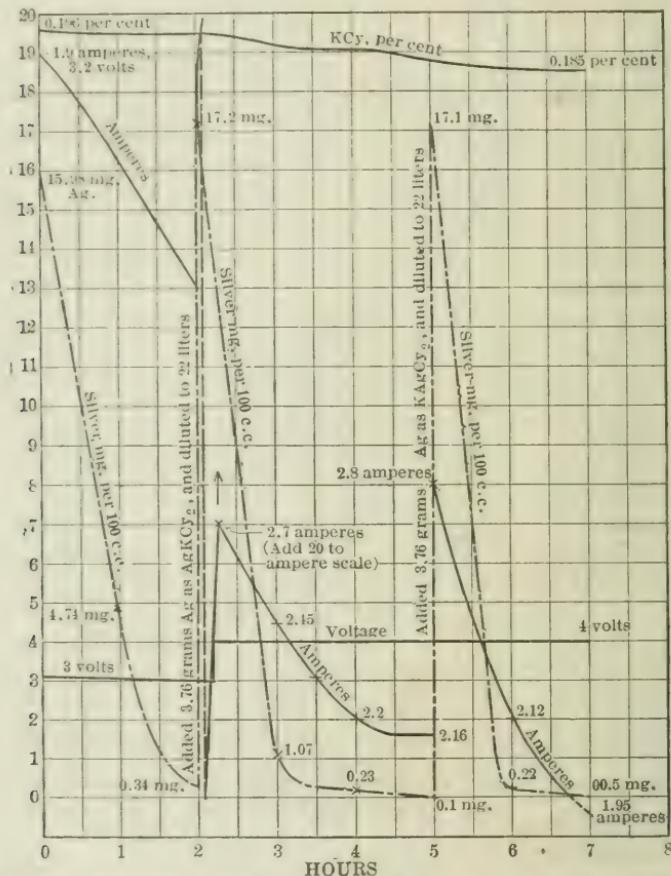


FIGURE 9.—Electrodeposition results with silver solution with rate of flow of 180 liters per hour; velocity, 20 inches per minute in open box, 45 inches through cathodes; 7 anodes of 8-mesh wire cloth; 40 cathodes of 30-mesh wire cloth; actual surface area, 6.38 square feet.

will be noticed that the precipitation curves show that the capacity of the box increased rapidly, a new charge being added at the end of two hours and another at the end of five hours. The voltage during the first two hours was 3, and during the rest of the time 4. The precipitation curves show successively better results.

As the precipitation became more effective, another feature noticed was that free cyanide was regenerated from the cyanide com-

bined with the precipitated silver. This feature was seen for the first time in the experiment represented in figure 10. In this experiment the flow of solution was increased to 300 liters per hour. The entire solution passed through the box 15 times in one hour. It will be

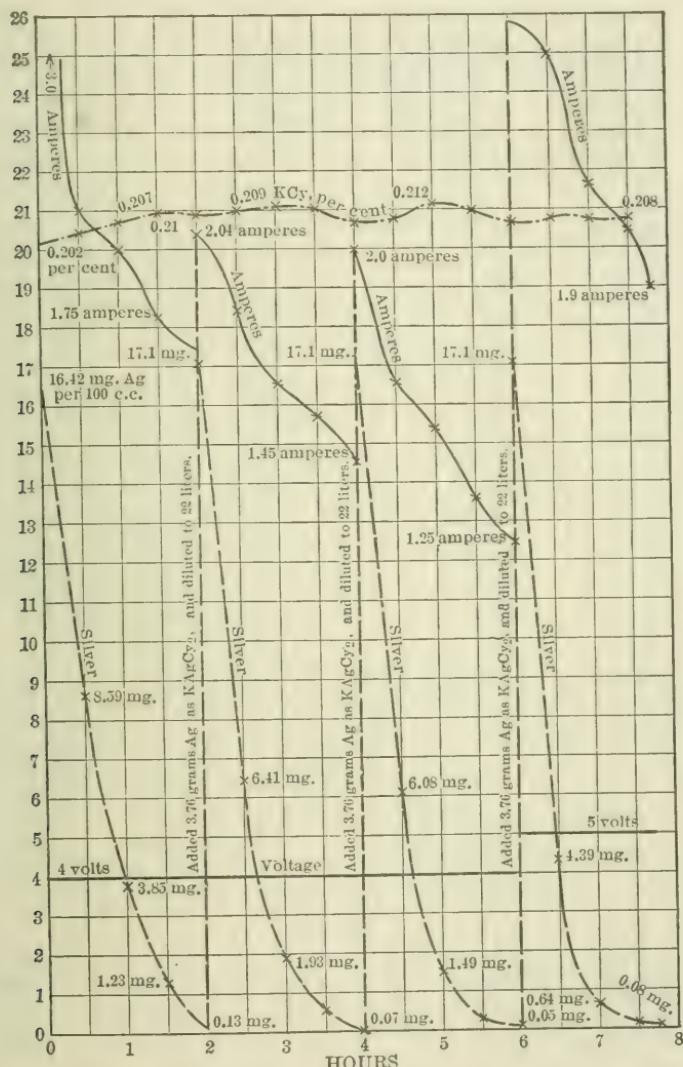


FIGURE 10.—Electrodeposition results with silver solution; rate of flow of 300 liters per hour; velocity through open box, 34 inches per minute; volume of solution, 22 liters; 7 anodes, 8-mesh wire cloth; 56 cathodes of 30-mesh wire cloth; wetted area, $3.5 \times 2.6 = 9.1$ square inches; actual surface area, 0.01773 square foot per square inch of cloth; for 56 cathodes, 8.936 square feet; length of electrodes, $5\frac{1}{4}$ inches; volume, 47.7 cubic inches or 0.782 liter.

noticed that at the end of every two hours a new charge of KAgCy_2 , with sufficient water to bring the volume up to 22 liters, was added

to the solution. The voltage was kept steady for the first six hours at 4, and during the last hour and a half was raised to 5 volts. It will be noticed also that the precipitation increased, especially between the sixth and seventh hours. The silver content and the current fell simultaneously, although the amperage did not fall quite as rapidly.

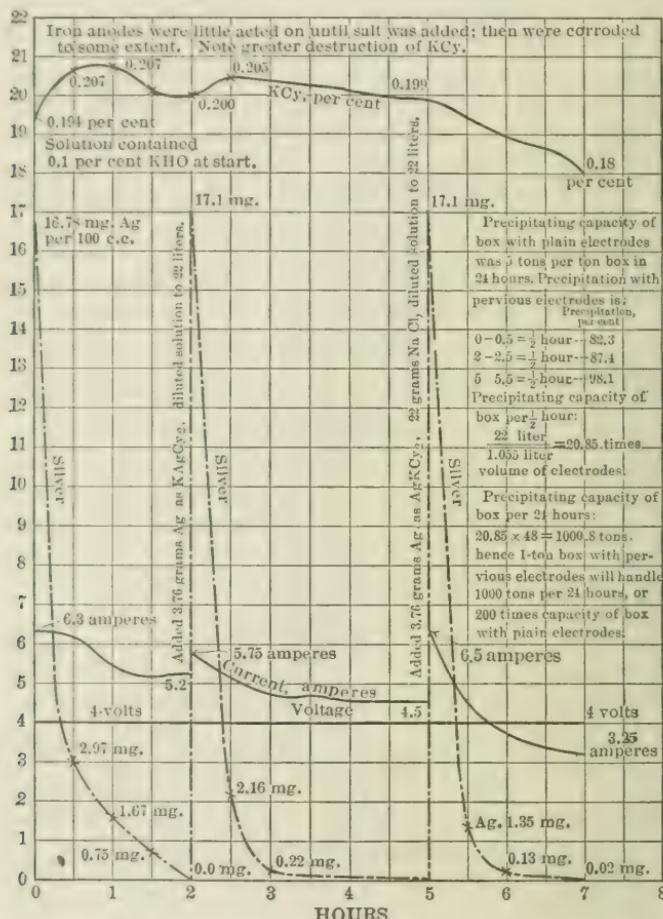


FIGURE 11.—Results of electrodeposition of silver with NaCl added to the solution; rate of flow, 300 liters per hour; velocity, 35 inches per minute through open box, 79 inches through cathodes; volume of solution, 22 liters; 11 anodes of 8-mesh wire cloth; 50 cathodes of 30-mesh cloth; total surface area, 5,735 square feet; length of electrodes, 18.75 cm.; volume occupied, 56.25 cm. or 1.055 liters.

as the silver content. It will be further noticed that during the rapid precipitation of the silver at the beginning of the experiment the solution contained 0.202 per cent cyanide, whereas at the end of one and one-half hours it had increased to 0.21 per cent. During the last half hour it fell again to 0.209 per cent. After a new charge of

KAgCy_2 , containing no free cyanide, had been added to replace the assay samples, the cyanide had again increased from 0.209 to 0.22 per cent, falling slightly again at the end of one and one-half hours, and rising each time a new charge of KAgCy_2 was added to the solution. There is no doubt about the titration of the cyanide.

The increase of cyanide during the precipitation period was seen still more clearly in the experiment represented in figure 11. The volume of solution and the rate of flow are the same as before. The number of cathodes is 50 and the voltage 4. Three charges of KAgCy_2 were treated, each containing 3.76 grams of silver. It will be noticed that during the first hour the cyanide had risen from 0.194 to 0.207 per cent, falling again in 30 minutes to 0.202 per cent as the silver was removed. When a new charge of silver cyanide was added it rose to 0.205, but fell at the end of three hours to 0.199 per cent. At the end of five hours a new charge of silver cyanide containing no free cyanide was added, together with 22 grams of salt. The salt was added to determine whether the increased conductivity of the solution, owing to the presence of the salt, would increase the rapidity of the precipitation. The salt did have somewhat such an effect. It will be observed, however, that there is a continued destruction of the cyanide by chlorine, resulting from the decomposition of the salt, which reduced the cyanide from 0.199 to 0.18 per cent.

CAPACITY OF BOX.

The estimated capacity of the box is shown in figure 11. The capacity of the box with plain electrodes without circulation, as already stated, was about 5 tons for a 1-ton box in 24 hours. In the first half hour, a precipitation of 82.3 per cent was obtained. In the first half hour of the second period a precipitation of 87.4 per cent was obtained, and in the first half hour of the third period the precipitation was 98.1 per cent. The volume treated was 22 liters, and the volume occupied by the 50 cathodes and 11 anodes was 1.055 liters. Dividing 22 by 1.055 we have for a half-hour period a precipitation capacity of 20.85 times the volume occupied by the electrodes, or 1000.8 for 24 hours. Clearly a box holding 1 ton, and fitted with electrodes as described, will handle over 1,000 tons in 24 hours. As a result of the investigation I was able to increase the precipitation capacity of the box filled with wire-cloth anodes and cathodes to more than 200 times that of a similar box with plain electrodes.

The effect of the increased capacity was shown still more strongly in the experiment represented in figure 12. The flow was increased to 720 liters per hour, and the voltage was increased to 9. The first treatment was for two hours, when 3.76 grams of silver was added to

replace the silver in assay samples. The recharging of the solution was repeated every hour for the next four hours, and the rapid regeneration of the cyanide is shown clearly by the upper curve. The rapid deposition of the silver is also shown, and the increased capacity of the box should also be mentioned.

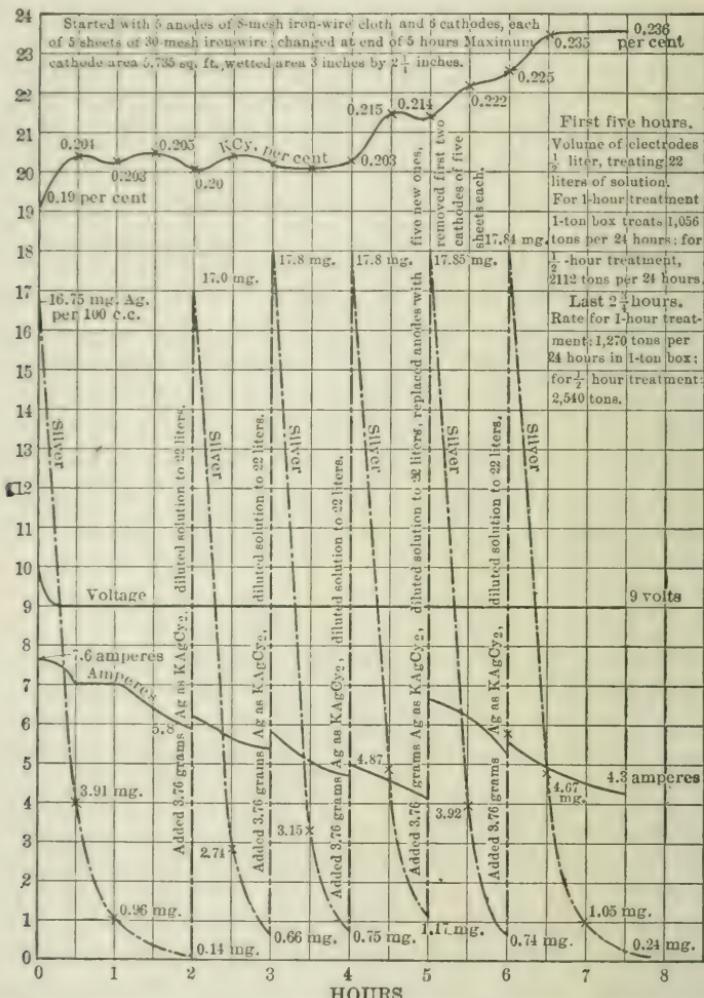


FIGURE 12.—Electrodeposition results with a rate of flow of 720 liters per hour; volume treated, 22 liters; velocity of flow, 84 inches per minute through open box, 189 inches through cathodes.

If the assay value of the solution be considered as reduced to about half an ounce of silver per ton, the capacity of the box can be figured at 1,056 tons per 24 hours for a 1-ton box; if the silver be considered to be reduced to a little more than an ounce per ton the capacity can be figured as 2,540 tons per 24 hours in a 1-ton box.

USE OF PEROXIDIZED-LEAD ANODES AND WIRE-CLOTH CATHODES.

In the preceding tests an important difficulty was encountered. The precipitation capacity of the box had been increased so rapidly that the 30-mesh wire cloth became clogged with precipitated silver, which interfered with the circulation of the solution. The wire-

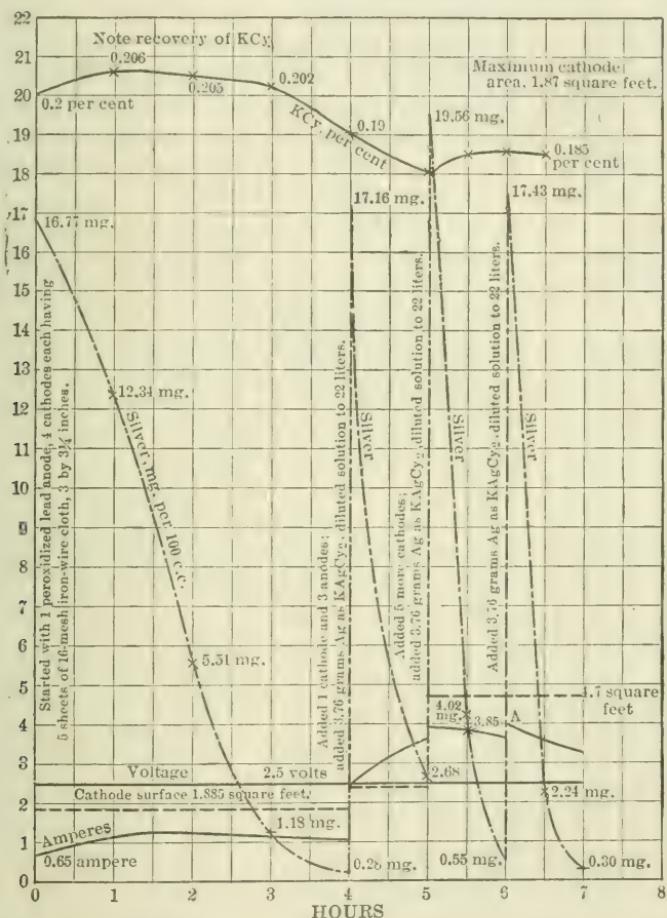


FIGURE 13.—Electrodeposition results with peroxidized-lead anodes and wire-cloth cathodes; volume of solution at start, 22 liters, containing 3.76 grams Ag as KAgC_2 , 22 grams KIO_3 , and 45 grams KC_2 ; rate of flow, 420 liters per hour; velocity through open box, 63 inches per minute; through cathodes, 142 inches.

cloth anodes also had become somewhat coated with ferric hydrate. An attempt was made to obviate these troubles.

I started with one peroxidized-lead anode, made of perforated sheet lead, and with four cathodes each formed from five sheets of 16-mesh iron-wire cloth, 3 inches wide and $2\frac{1}{4}$ inches deep in the solution, a new box having been made for the purpose. The rate of flow was 7 liters per minute, or 420 liters per hour. With only one

peroxidized-lead anode and with 20 sheets of wire-cloth cathodes, 10 on either side of the anode, the precipitation was naturally not so rapid as it had been when more cathodes were used. The wire cloth had a cathode area of 1.885 square feet. The voltage was $2\frac{1}{2}$ during the entire experiment. The results of the test are shown in figure 13. It will be noticed that the number of amperes, which at the start was 0.65, increased during the first hour and a half to 1.3, and slowly fell again to about 1 during the remainder of the four hours.

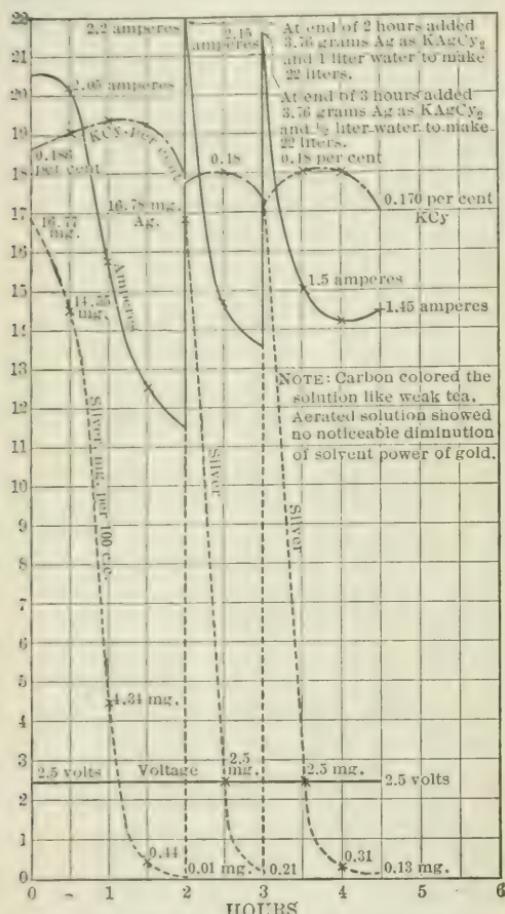


FIGURE 14.—Electrodeposition results with carbon anodes and addition of KIO to the solution: 22 liters of solution used, containing 45.5 grams KCy , 22 grams KIO , and 3.76 grams Ag as $KAgCyg$; rate of flow, 360 liters per hour; velocity through open box, 42 inches per minute; through cathodes, 95 inches; anodes kept 4 days in melted vaseline; each consisted of 7 $\frac{1}{2}$ -inch "Electra" carbon rods, spaced $2\frac{1}{2}$ inches apart, immersed to depth of $2\frac{1}{2}$ inches; 14 cathodes, each being 5 sheets of 16-mesh iron wire cloth; total area, 6.59 square feet.

the solution had been reduced from 16.77 to 0.28 mg. per 100 c. c. (0.09 ounce per ton). At this point another bunch of five 30-mesh wire-cloth cathodes, making 25 in all, were added, also three perforated, peroxidized-lead anodes, making 4 in all. Then another charge of

amperes, which at the start was 0.65, increased during the first hour and a half to 1.3, and slowly fell again to about 1 during the remainder of the four hours. The reason for the anomaly was that the conducting surface of the cathodes became covered with a film of iron rust which prevented contact with the solution.

At the end of two hours the solution seemed to be saturated with gas, most of which, however, was oxygen set free at the anode. Almost no evolution of gas was visible at the cathode. At the end of three hours, although only the single anode was used, placed between two "bunches of five" cathodes the solution thus traversing ten thicknesses of wire cloth, the upstream sides of the cathodes, which received the richest solution, were almost thoroughly coated. At the end of four hours the silver content of

silver cyanide and water was added to make 22 liters. The cathode surface had been increased to 2.4 square feet and the precipitation was much more rapid than before. At the end of the fifth hour the number of cathodes was increased to 10 bunches of five each, or 50 in all. A new charge of silver cyanide was then added. The cathode surface having been increased to 4.7 square feet, the rate of precipitation had increased so rapidly that the silver content was reduced in 1 hour from 19.5 to 0.55 mg. per 100 c. c. A new charge of silver cyanide was again added, bringing the silver content up to 17.43 mg. per 100 c. c., but the precipitation of silver was so rapid that in 1 hour the silver content was reduced to 0.3 mg. per 100 c. c., or about 0.1 ounce per ton.

USE OF CARBON ANODES.

The next point tested was the effect of using carbon anodes, while employing the same box as before, and treating a solution similar in volume and content, but containing 10 per cent of 1 per cent caustic potash solution. The rate of flow was 6 liters per minute, or 360 liters per hour. The anodes were made of electric-light carbons, and in order to protect these from the action of oxygen they were soaked four days in melted vaseline. The form of the anodes was that of a comb, seven carbons being fastened together by means of a conducting strip of lead. The carbons, each three-eighths of an inch in diameter, were spaced one-eighth of an inch from one another and were immersed in the solution to a depth of $2\frac{1}{2}$ inches. There were 14 cathodes of five bunches each, formed of 16-mesh wire cloth, and having a total area of 6.59 square feet. The voltage was kept at $2\frac{1}{2}$. Precipitation curves for this experiment were obtained in a manner similar to those for previous experiments. The continued parallelism of the ampere curve and of the silver-precipitation curve is still observed. The cyanide recovery during the rapid precipitation of the silver, and the cyanide destruction after precipitation, are clearly shown in the curves. The carbon anodes were only slightly acted on, though the solution became of the color of weak tea. The solution, after having been aerated, showed no noticeable diminution of solubility for gold.

THE USE OF UNCOATED CARBON ANODES.

The next set of experiments was undertaken to determine whether or not ordinary electric-light carbons which had not been treated with vaseline could be used, and to determine the voltage required for effective precipitation. A set of the uncoated, electric-light, carbon-anode combs, such as have been described, were used, and also the same cathodes, in 14 bunches of five, making 70 in all. The cathodes were already coated with silver from the preceding experi-

ment. At first only 1 volt was applied, and instead of getting precipitation of silver, the silver already precipitated redissolved, as can be seen from the silver-precipitation curve in figure 15. The curve starts at 16.78 mg. per 100 c. c., and rises to 25 mg. per 100

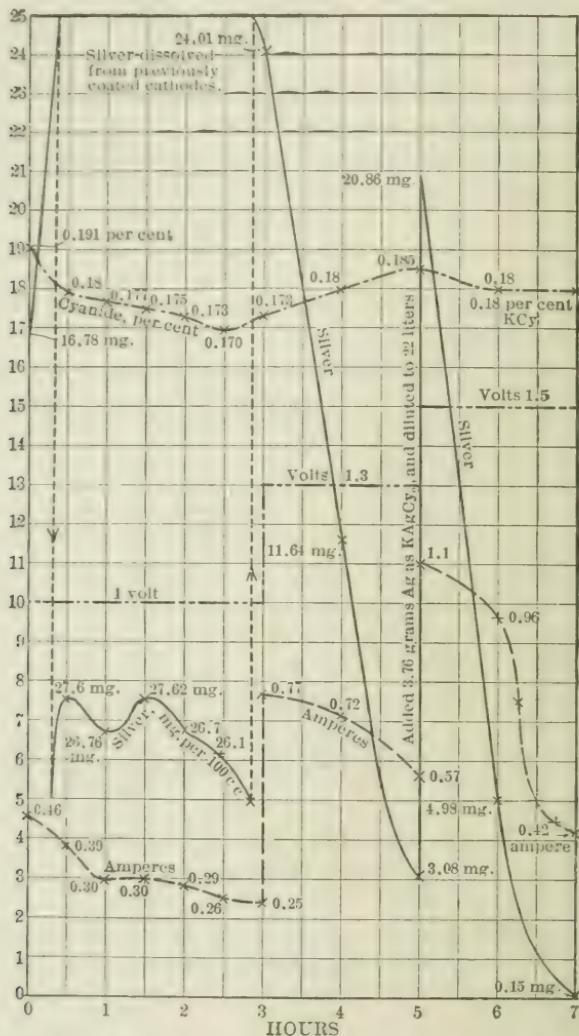


FIGURE 15.—Electrodeposition results with carbon anodes not coated with vaseline: 22 liters of water used, containing 44 grams KC₂, 22 grams KIO₃, 3.76 grams Ag as KAgC₂; rate of flow, 330 liters per hour; velocity through open box, 42 inches per minute; through electrodes, 96; 6 anode "combs" and 70 cathodes (same as in fig. 14) used; cathode area, 6.6 square feet. Owing to low voltage or poor contacts, some Ag was redissolved during first part of test and KC₂ absorbed.

c. c. in the first few minutes, then continues to rise and indicates 27.6 mg. per 100 c. c. at the end of the first quarter of an hour. The silver then decreased to 26.76 mg., increased again to 27.62, and fell again at the end of 2½ hours to 25. At the end of 3 hours the volt-

age was increased to 1.3 volts. At this point, the content of silver, which originally had been only 16.78 mg., had increased to 24 mg. With 1.3 volts, the silver began promptly to come down, and at the end of the next two hours the silver content had decreased to 3.08 mg. when a new charge of silver cyanide was added, bringing the content up to 20.86 mg. The voltage was increased to $1\frac{1}{2}$ volts, whereupon the silver was rapidly precipitated, being reduced in two hours to 0.15 mg., or about 0.05 ounce per ton. It will be noticed that during the whole time that silver had been dissolving from the cathode, free cyanide had been falling simultaneously. As soon as the silver began to be precipitated, it rose again, and at the end of the process, the cyanide content, which originally was 0.191 per cent, had fallen to 0.18 per cent. The experiment clearly shows that 1 volt is not sufficient for the effective precipitation of silver, that 1.3 volts is the minimum, and that a higher voltage than this is better.

EXPERIMENTS ON THE REGENERATION OF CYANIDE.

I have already called attention to the regeneration of the cyanide combined with the silver to be precipitated. The following experiments were undertaken to study the matter further. It was desired to avoid the oxidation of cyanide at the anode as much as possible; accordingly only $1\frac{1}{2}$ volts was employed. The solution used on a previous day was brought to a volume of 22 liters by adding the requisite amount of water. It then contained 0.189 per cent KCy and 0.1 per cent KHO. The rate of flow was 480 liters per hour. The electrodes occupied about 1 liter of space. The same anodes and cathodes were used as before (see fig. 14). The results of this test are shown in figure 16.

At the end of the first hour it is seen that the silver content had fallen from 17.36 mg. per 100 c. c. to 4.58 mg. leaving only about 1.74 ounces per ton in solution. Then a new charge of 3.76 grams of KAgCy₂ was added, and sufficient water to bring the volume back to 22 liters after the samples had been taken out. This brought the silver content up to 21.64 mg. per 100 c. c.

At the end of the second hour the silver content had fallen to 2.29 mg. per 100 c. c., or about 0.78 ounce per ton. A new charge of silver was added, as before, and at the end of the third hour the silver content had fallen to 0.74 mg. per 100 c. c., or 0.25 ounce per ton. A new charge was then added, and at the end of the fourth hour the silver had been reduced to 0.6 mg. per 100 c. c., or to 0.2 ounce per ton. A new charge of silver was then added, and at the end of the fifth hour the content had fallen again to 0.28 mg. per 100 c. c., or to 0.09 ounce per ton. A new charge was then added, and at the end

of the sixth hour the content had again fallen to 0.7 mg. per 100 c. c., or to 0.25 ounce per ton. A new charge was then added, and at the end of the seventh hour the content had been reduced to 0.33

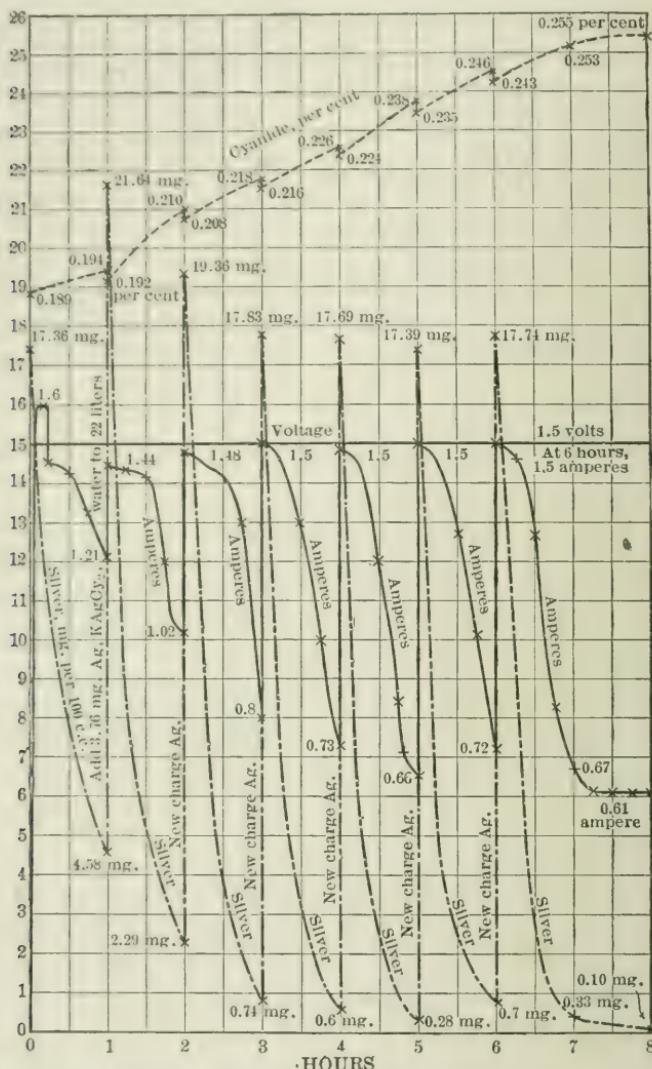


FIGURE 16.—Electrodeposition results showing regeneration of cyanide. Eight liters of water added to previously used silver cyanide solution to make up 22 liters, containing about 22 grams of KIO_3 . Anodes and cathodes same as in fig. 15. Rate of flow, 480 liters per hour; velocity per minute through open box, 56 inches; through cathodes, 127. At 1, 2, 3, 4, 5, and 6 hours added 3.76 grams Ag as $KAgCy$ and 0.25 liter of water to bring volume up to 22 liters. Note recovery of cyanide.

mg. per 100 c. c., or 0.11 ounce per ton. The test was continued for another hour, at the end of which time the silver in solution had been reduced to 0.1 mg. per 100 c. c. or 0.03 ounce per ton.

It will be observed that the cyanide titration shows a continuous rise in cyanide content. At the start the cyanide content was 0.189 per cent, and at the end of the first hour it had risen to 0.194 per cent, dropping again on account of dilution with water to 0.192 per cent. At the end of the second hour it had risen to 0.21, dropping again by dilution to 0.208. At the end of the third hour it had risen to 0.218, dropping again by dilution to 0.216. At the end of the fourth hour it had risen to 0.226, dropping again by dilution to 0.224. At the end of the fifth hour it had risen to 0.238. At the end of the sixth hour it had risen to 0.246, again dropping by dilution to 0.243. At the end of the seventh hour it had risen to 0.253, and at the end of the eighth hour it had risen to 0.255 per cent.

The total actual rise in the cyanide content, as shown by titration, was 0.066 per cent. If to this be added the amount of cyanide in the quantity of solution taken out for the assays, which was about 250 c. c. each time, the total saving of cyanide is 0.084 per cent. Multiplying this result by the weight of the solution, taken as 22 kg., gives an actual saving of 18.48 grams KCy, which was formerly combined with about 22.56 grams of silver. Taking the molecular weight of KCy as 130 and the atomic weight of silver as 108, if all the cyanide had been recovered there would be 1.2036 grams of KCy for every gram of silver precipitated. On this basis, as there was, roughly, 22.56 grams silver precipitated, there would be saved 27.07 grams KCy. The amount actually recovered was 18.48 grams, or slightly more than 68 per cent of the cyanide originally combined with the silver. It is evident, therefore, that all of this cyanide was not recovered, but a sufficient amount was saved to make this saving a highly important factor in the cost of precipitation.

It will be noticed that the curves representing the cyanide content all are rising where the silver is being rapidly precipitated. Between the sixth and seventh hour, and particularly at the end of the seventh hour, the curve of the recovered cyanide rises more rapidly than later, when the silver has been mostly precipitated. Toward the end of the experiment the destruction of cyanide begins to prevail over the regeneration, whereupon the curve rises more slowly, and finally begins to fall. This is caused by oxidation, which is constantly taking place at the anodes.

Attention is particularly directed to the parallelism between the fall of the ampere curves and those showing the precipitation of the silver. This is most clear between the sixth and eighth hours, where the ampere curve falls abruptly from 1.5 amperes. When the silver has fallen to 0.2 mg. per 100 c. c., and has been practically exhausted, as at the end of $7\frac{1}{4}$ hours, the ampere curve has fallen to 0.61. Here it remains constant during the rest of the experiment.

This phenomenon suggests a very simple method of controlling the precipitation without assaying the solution. If the voltage is maintained constant, the ampere curve shows the critical point at which it is best to stop precipitation. The point at which the ampere curve becomes constant is the most economical point to stop precipitation. At this point the recovery of cyanide reaches the maximum, and a further continuation of precipitation is wasteful of electric current.

During this test assay samples were taken every 15 minutes, but in practice sampling at longer intervals would suffice to correct the reading of the ammeter. This method of controlling the work I consider to be of great practical importance industrially, and the benefit can be gained only where a large volume of solution which is being rapidly circulated is treated, as here shown. The subject of cyanide regeneration is considered more fully in subsequent pages.

RUSTING OF IRON-WIRE CATHODES.

Attention should be called to another point that is evident in nearly all the later tests, but is also shown very clearly in the foregoing experiment. As the experiments were conducted intermittently and could only be carried on in the daytime, between the tests the wire-cloth electrodes became more or less rusted by the action of moisture on the wires, which were coated with silver. As is well known, under such circumstances a local action sets in, which causes rusting of the iron wire. When the cathodes were first immersed in the solution, much of the electric current was consumed in reducing this oxide of iron, and hence was not available for the precipitation of silver. It will be noticed that the precipitation improves during the continuation of the process. Other causes of this increase, aside from the dissolution of the rust, are that the conductivity of the solution gradually increases, owing to the presence of a larger amount of cyanide and other salts, and that the surface of the wire-cloth cathodes becomes covered with silver, making them better electrical conductors. From these three reasons it is evident that the rusting of the wire cloth will not take place whenever it is possible to have the process in continuous use.

TREATMENT OF RICH SILVER CYANIDE SOLUTIONS.

EXPERIMENT WITH SODIUM CHLORIDE IN THE SOLUTION.

The experiments hitherto described were conducted with silver solutions that were comparable in richness with those that occur in the treatment of ordinary ores. Experiments were next undertaken with a richer solution, containing 119.11 mg. of silver per 100 c. c. (see fig. 17), or about 41 ounces per ton. In other respects the solu-

tion treated was similar to those used before, consisting of 22 liters of 0.1 per cent free KHO, with 0.237 per cent KCy. In order to increase the conductivity of the solution, about 1 per cent of NaCl was added, and the circulation was at the rate of $9\frac{1}{2}$ liters per minute, or 570 liters per hour. Six uncoated carbon anode combs were used; also 14 "bunches of five," or 70 in all, of the 16-mesh iron-wire cathodes, with a total area of 6.6 square feet. The voltage was 1.5.

Regeneration of the cyanide reached a maximum in this experiment at the end of two and one-half hours, when the cyanide content had risen to 0.295 per cent, after which it slowly declined to 0.273 per cent, owing to the action of chlorine and oxygen, set free at the anode. It will be noticed that there is again a close parallelism between the ampere curve and that of the rate of precipitation of the silver. Both curves change direction rapidly a little after three hours, the amperage falling from 2.57 to 0.70 at the end of that time, and the silver from 119.11 to 2 mg.

The effect of stopping circulation of the solution is shown at the end of three and one-fourth hours, at which time the belt on the pump accidentally broke. The current immediately dropped from 0.73 to 0.65, rising again to its place on the curve as

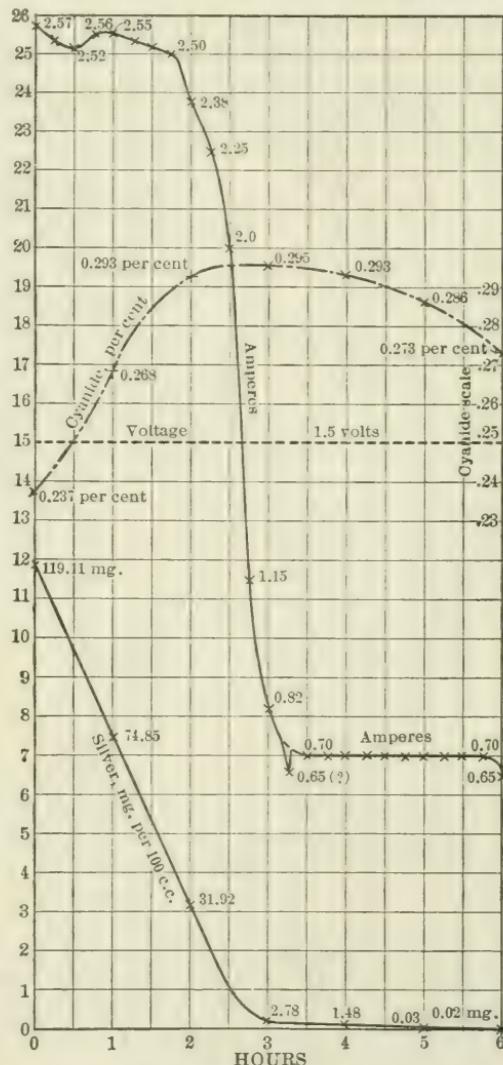


FIGURE 17.—Electrodeposition results with richer solution. Twenty-two liters of solution, containing 119.11 mg. of silver, 22 grams KHO, 220 grams NaCl, and 0.237 per cent KCy. Six uncoated "Electra" carbon anode combs. Cathodes, 14 bunches of 5 each, of 16-mesh wire cloth; total area, 6.6 square feet. Rate of flow, 570 liters per hour; velocity through open box, 66 inches per minute; through cathodes, 150.

soon as the pump was started. At the end of five and three-fourths hours, the circulation being maintained, the current was 0.70, and when the circulation was stopped it fell at once to 0.65.

EXPERIMENT WITHOUT SODIUM CHLORIDE.

In order to determine whether the use of salt in the solution was beneficial the experiment was repeated without salt. The same vol-

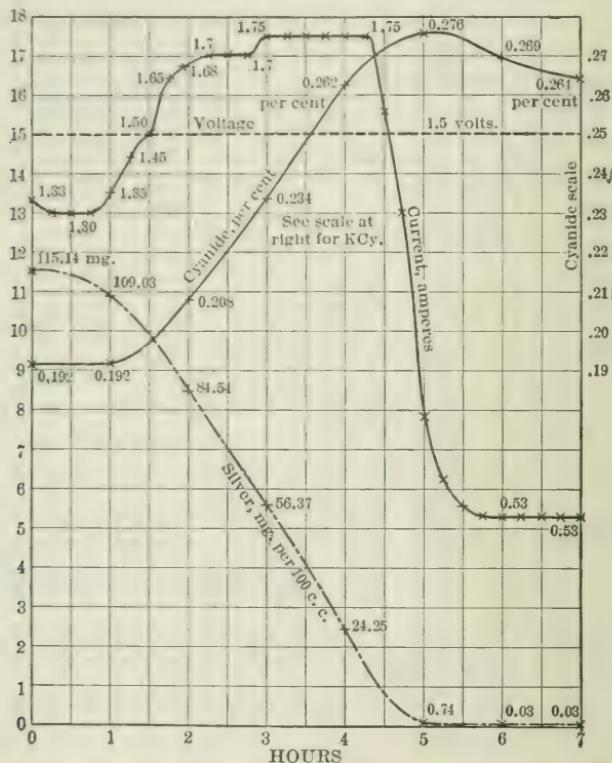


FIGURE 18.—Electrodeposition results with rich silver solution and no NaCl. Solution, 22 liters, containing 42.24 grams KCy, 25.33 grams Ag as KAgC_2 , and 22 grams KHO. Rate of flow, 540 liters per hour; velocity per minute through open box, 63 inches; through cathodes, 141. Anodes and cathodes same as in figure 17; cathodes were coated with silver and rusted from standing over night after removal from the salt solution used in the previous test.

ume of solution, containing 0.1 per cent KHO and 0.192 per cent KCy and 115.14 mg. of silver per 100 c. c. was used. The flow was 540 liters per hour. The same cathodes, which had been coated with silver, were used as in the previous experiment (fig. 17). The results of the test are shown in figure 18. The ampere curve was decidedly different in form from that of the former experiment. It started at 1.33 amperes, falling in one-fourth hour to 1.30, then rising rapidly to 1.75 at the end of three hours. This value it main-

tained until four hours and twenty minutes of the total period had passed, when it fell precipitately until, at the end of five and three-fourths hours, it had become 0.53 ampere. There it remained constant until a total of seven hours had passed, when the experiment was stopped. It will be noted that the increase of cyanide content did not begin until one hour had passed, when it rose from 0.192 to 0.276 per cent. At this point most of the silver had been precipitated. At the end of five and one-half hours the cyanide content began to fall, and at the end of the test was 0.264 per cent.

It is evident from a study of these curves that the experiment should have been stopped at the end of five hours, when the recovery

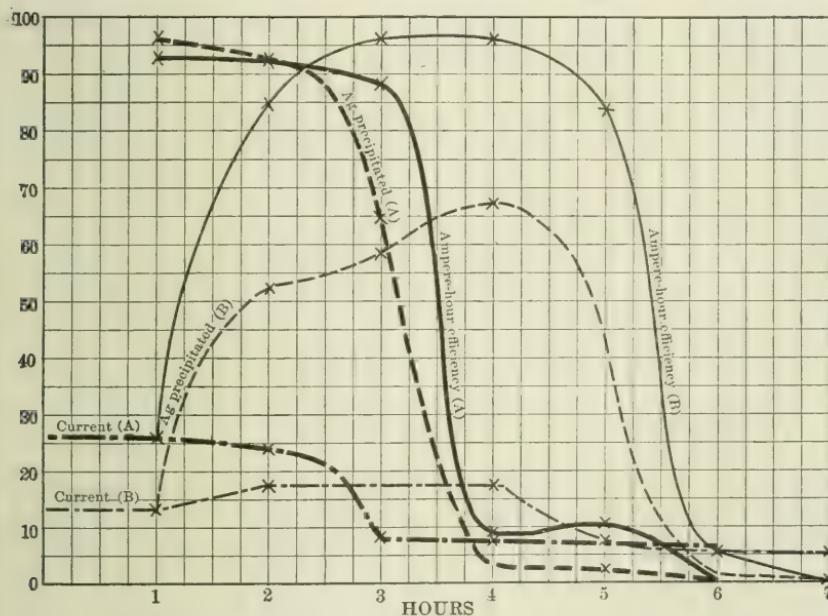


FIGURE 19.—Results of tests with and without use of salt compared. A, curves from test shown in fig. 17, salt used. B, curves from test shown in fig. 18, no salt used.

of cyanide was at the maximum. After that time the current was not used economically, and little silver was precipitated. The irregular rise of the current was evidently due to the rusting of the cathodes, which had stood over night wet with salt solution. The silver did not begin to come down rapidly, and the cyanide to be regenerated, until this rust had been reduced by the current. If the cathodes had been perfectly free from rust no doubt the current would have started at about 1.75 amperes, and would have remained nearly constant, and the silver would have been precipitated much earlier in the experiment. The voltage and amperage were read every 15 minutes with Weston standard meters. At the start and at the end of each hour a 250-c. c. sample was taken for cyanide titrations and for silver

assays. It will be observed that the electrical efficiency was extremely high as long as there was any silver to be precipitated, but that it fell rapidly when the silver content became diminished. The relative efficiency in the two tests is best shown in figure 19.

COMPARISON OF RESULTS.

If, neglecting the oxidation at the anode, we assume that the silver is precipitated at the cathode by the potassium ion, then for every atom of silver precipitated there will be two molecules of KCN set free at the cathode. Assuming 65 as the molecular weight of KCN, for every 108 grams of precipitated silver 130 grams of KCN should be regenerated, or $\frac{130}{108} = 1.2036$ grams of KCN regenerated for each gram of silver precipitated. Evidently, notwithstanding the initial resistance to the current due to the rusting of the anodes, the final efficiency of both the silver precipitation and the cyanide regeneration was better in the second experiment, shown in figure 18, than in the first, shown in figure 17. In the first experiment the highest silver efficiency was 93.62 per cent, whereas in the second it was 96.35. In the first the highest cyanide regeneration was 58.19 per cent, but in the second it rose to 76.67 per cent. Evidently the addition of sodium chloride is not justifiable. The irregularity of the curves in the second experiment was also due to this cause.

THEORY OF ELECTROLYTIC CYANIDE REGENERATION.

The theory of electrolytic regeneration of cyanide is of great practical importance and is difficult to explain in a few words. According to the modern view the ions that carry the current in the solution exist already dissociated, or, at most, loosely associated. The electric current, accordingly, has only to direct their motion. The anode, being the positive pole of the cell, attracts the anions, each of which carries a negative charge to the anode where it gives up its negative charge. Simultaneously the cathode, being the negative pole of the cell, attracts the cations, each of which carries a positive charge and delivers it to the cathode. By this means each of the ions travels through the solution a variable, relative distance dependent on the "transfer velocities." The velocities have been accurately measured by Hittorf and others for many electrolytes. They are not necessarily equal; often they are relatively quite different; but for simplicity let us assume that all are equal. The potassium cation and the chlorine anion in normal solutions of KCl have nearly equal values.

Let us first assume a solution containing ions arranged as shown in the following diagram:

	+		+		+		+		+		+	
1	2	3	4	5	6	7	8	9	10	11	12	13

In this arrangement the + sign represents, for example, the potassium ion with its positive charge, the — sign represents the chlorine ion with its negative charge. If into such a solution are inserted two platinum electrodes with + and — charges the equilibrium is disturbed and the anions with their negative charges move one place to the right toward the anode with its negative charge, and each cation moves one place to the left with its positive charge, toward the cathode with its negative charge. The arrangement then becomes as follows:

-		+	-	+	-	+	-	+	-	+	-	+
1	2	3	4	5	6	7	8	9	10	11	12	13

When the chlorine anion, with its negative charge, reaches the anode, it gives up this electrical charge and becomes gaseous chlorine which escapes. When the potassium cation with its positive charge reaches the cathode it gives up its positive charge and becomes metallic potassium, which by a secondary reaction decomposes the adjacent water and produces KHO which remains in solution and hydrogen gas which escapes as such. It will be noticed that the intervening solution remains unchanged in chemical composition and that the only chemical changes occur at the electrodes. The theory thus agrees with the facts first observed by Faraday.

As regards potassium silver cyanide, the potassium cation with its positive charge travels a little faster than the AgCy_2 anion with its negative charge. The difference of velocity is not great and the preceding diagram will suffice to explain the case. We have only to suppose the cation with the + sign to be potassium as before and the anion with the — sign to be not chlorine but AgCy_2 . There will then be an increase of one molecule of AgCy_2 at the anode and an increase of one atom of potassium at the cathode. Suppose that there also are evenly diffused through the solution other molecules of KCy, KHO, KAgCy_2 , not yet brought under the influence of the current. Then when a K cation reaches the cathode and gives up its positive charge

it finds KAgCy_2 , there, which is more easily decomposed than water. A secondary action, shown in the equation following, is then supposed to ensue.



This reaction was first suggested by Hittorf to explain the smooth, silver deposit obtained from cyanides, in contrast with the loose crystalline deposit from other salts of silver, such as the nitrate, where the silver is directly deposited by the current.

It will be noted that after electrolysis two atoms of silver are removed from the solution at the cathode, one by electrolytic wandering to the anode, the other by the precipitating action of the cation. (As regards the nitrate there would be removed only the one atom directly precipitated in crystalline form by the electric current.)

Let us next suppose this process to be repeated at the cathode, and further, that throughout the solution, not yet affected by electrolysis, there is uniformly diffused 2 KCy in the free state, 2 KHO, and 2 KAgCy_2 . At the cathode there is, then, before electrolysis: $2\text{KCy} + 2\text{KHO} + 2\text{KAgCy}_2$, and after electrolysis (as 2 K ions appear): $2\text{KCy} + 2\text{KHO} + 2\text{KAgCy}_2 + 2\text{K} - 6\text{KCy} + 2\text{Ag} + 2\text{KHO}$. It is seen that there is a gain at the cathode of 4 KCy, free, for each 2 Ag precipitated.

Let us make a similar supposition concerning the solution at the anode. Before electrolysis the composition was, $2\text{KCy} + 2\text{KHO} + 2\text{KAgCy}_2$, and after two units of electricity have passed, it is $2\text{KCy} + 2\text{KHO} + 2\text{KAgCy}_2 + 2\text{AgCy}_2$, an increase of two molecules of AgCy_2 at the anode. Now as shown by Morgan, 2AgCy_2 easily splits up into $2\text{AgCy} + 2\text{Cy}^a$.

The 2AgCy easily combines with 2KCy to form 2KAgCy_2 , and the 2Cy reacts with 2KHO to form H_2O , KCyO , and KCy , one half being destroyed by becoming cyanate, the other half being regenerated as KCy . Combining these reactions at the anode into one we have, after electrolysis, the following chemical substances: $4\text{KAgCy}_2 + \text{KCyO} + \text{KCy} + \text{H}_2\text{O}$. Hence at the anode there is a gain of two molecules of KAgCy_2 , one of KCyO , one of water, a loss of two molecules of KHO and two of KCy , and a gain of one molecule of KCy ; therefore there is a net loss at the anode of KCy . But there was a gain at the cathode of 4 KCy , hence the net result is a total gain of 3 KCy for each 2 Ag precipitated, and the weights of silver precipitated and cyanide recovered will be:

$$\frac{\text{Cyanide recovered}}{\text{Silver precipitated}} = \frac{3 \times 65}{2 \times 108} = \frac{195}{216} = 90.27 \text{ per cent.}$$

^a Christy, S. B., Electromotive force of metals in cyanide solutions: Trans. Am. Inst. Min. Eng., vol. 30, 1900, p. 882.

If no cyanide were oxidized, for every part of silver precipitated here would be: $\frac{2 \times 65}{108} \times 100 = \frac{130}{108} \times 100 = 120.37$ per cent cyanide recovered. As will be seen later, by greatly increasing the cathode area as compared with the anode area, I have actually recovered free cyanide to the extent of 118 per cent of the weight of the silver precipitated.

The reactions with potassium auro-cyanide are exactly the same as with those of silver, AuCy_2 being substituted for AgCy_2 . (It is possible that auric-cyanides are formed at the anode to be afterwards reduced to aurous at the cathode.) As the atomic weight of gold is greater than that of silver, however, the relative weights of cyanide recovered from a given weight of gold will be $\frac{108}{197} = 0.55$ times the amount recovered by an equal weight of silver. Further, as gold solutions usually contain very little gold cyanide compared with those obtained in treating rich silver ores, the amount regenerated is seldom noticeable.

Theoretically, cuprous cyanide should permit a large regeneration of cyanide, owing to its low atomic weight. I have been unable to obtain certain proof of this regeneration in the few experiments I have tried. Mr. Hamilton, in experiments with the Butters process, claims to have obtained such evidence. I shall discuss this later. The facility with which both gold and copper form complex cyanides of higher valency at the anodes by taking on one or more Cy radicals possibly explains the greater difficulty of regenerating cyanide from them than from silver cyanides. With regard to possible regeneration of cyanide from potassium cyanate and sulpho-cyanate, as claimed by Clancy, I will say that many years ago I made some preliminary experiments on this subject and got some small traces of regeneration, but not enough to cause me to follow the matter further. The regeneration of cyanide up to 118 per cent of the weight of silver precipitated as previously described would seem to indicate that some of the cyanate must have been regenerated.

Evidently, there is the certain possibility of regenerating a large part of the cyanide combined with silver, particularly in the rich solutions. This gives to electrolytic methods a great advantage over the usual methods of zinc precipitation. But to take full advantage of such regeneration the silver precipitation must not be pushed too far, for when the silver is nearly gone, electric current is wasted in decomposing the water, and the nascent oxygen set free at the anode destroys more cyanide than is regenerated at the cathode, particularly when the surface of the anode equals or exceeds that of the cathode. Of course actual mill solutions contain many other substances than those I have supposed, and the reactions are much more complicated

than those I have outlined. The final result depends not only on the composition of the solution, but also on the voltage, the relative current density at anode and cathode, and even on the physical as well as the chemical nature of the cathodes themselves. The tendency of cyanogen molecules to combine with one another, forming para-cyanogen, and to oxidize to azulmic acid is another complication, as is the tendency, which should be mentioned, of cyanide to deteriorate into K_2CO_3 and ammonia compounds. The presence of sufficient free alkali is of controlling importance in the regeneration of the cyanide.

CAN CYANIDE BE REGENERATED BY THE ELECTROLYSIS OF FERROCYANIDES?

Prof. Kern,^a of Columbia, in a report published in 1913, answers this question with an emphatic "No!" He says:

(12) The regeneration of cyanide solutions which contain sulphocyanide and ferrocyanide does not occur by electrolysis by direct current, whether the conditions of electrolysis be made oxidizing or reducing by varying the relative current densities at the anode and the cathode.

On March 14, 1901, I made a preliminary investigation to see whether there was anything in this idea. Twelve liters of a 1 per cent solution of K_4FeCy_6 , with 0.2 per cent KHO, was made up. It was circulated through the deposition box. Six hard carbon comb anodes were used and 14 of the 5-cluster clean iron-wire cathodes.

The original solution was carefully titrated for KCy and appeared to contain a trace (0.001 per cent) of KCy, which possibly was produced by the action of the potash. The solution was clear and of a pale yellow color. It was electrolyzed for four hours at 1.5 volts, and 1.4 to 2.1 amperes. The solution changed in color, taking on a slightly greenish tinge, and traces of a deposit like Fe_3O_4 formed on the carbon anodes. Seemingly there was a very slight increase in the reaction for cyanide, but this was doubtful.

The carbon anodes were then removed and platinum was substituted for them. The voltage was increased to 2.5, and the current of 3.3 to 4.2 amperes was continued for one hour. No definite change was observed in the cyanide. A little ferric hydrate and Prussian blue formed on the anodes.

The voltage was then raised to 4, and the current increased to 8 amperes and was continued for one hour. The solution was now full of fine bubbles and had turned orange color, due probably to suspended ferric hydrate. A distinct reaction for cyanide was obtained, the titration showing 0.005 per cent KCy. The anodes were coated with ferric hydrate and Prussian blue. In 20 minutes more

^a Kern, E. F., *Electrolysis of cyanide solutions*: *Trans. Am. Electrochem. Soc.*, vol. 24, 1913, p. 265.

the KCy content rose to 0.007 per cent, and one hour later to 0.019 per cent. The entire solution was full of minute bubbles of gas, the composition of which was not determined. Also, loose flocculent ferric hydrate was contained in suspension. Of the original sample, which titrated 0.001 per cent KCy before electrolysis, 22 c. c. was inclosed in a tube with 12 c. c. of air and with a standard gold strip 2 inches by one-fourth inch in size, weighing 0.25 gram. The gold strip was then rotated for one hour in the solution, after which time it was found to have lost in weight 0.25 mg. gold. The solution therefore must have contained a trace of cyanide produced by the dissociation of the ferrocyanide in the presence of the KHO.

A similar experiment was made with 22 c. c. of the clear solution (titrating 0.019 per cent KCy), taken at the end of the electrolysis, and 12 c. c. of air. Both tubes containing the gold were rotated on the same shaft for one hour side by side. Upon weighing the gold, the loss from this second strip was 4.05 mg., or more than 16 times that from the first strip.

The gold strips were then reversed, the second being placed in the original solution and the first in the residual solution. The former now lost 0.04 mg. and the latter 0.94 mg. A film, not visible to the eye, seemed to have formed on both gold strips, but the electrolyzed solution was still leading, being this time 23.5 times as effective as the original solution. It would appear from these experiments that with platinum electrodes, at least, cyanide can be regenerated from potassium ferrocyanide in the presence of caustic potash, with a current of moderate density. This would give a great advantage to electrolysis if it could be made generally applicable. However, I did not follow the matter further.

Although Kern denies the possibility of any regeneration from the ferrocyanide by direct current, he says:^a

When cyanide solutions containing sulpho or ferrocyanide were electrolyzed, the cyanide consumption was much less than that which occurred in pure cyanide solutions, which indicates that sulphocyanide and ferrocyanide act as protective agents during the electrolysis of cyanide solutions.

It would seem that another explanation than that of "protective agents" is possible—namely, that there was actually a slight regeneration that partly offset the usual oxidation losses. The amount of cyanide that was regenerated in my test was slight. It was necessary to use 100 c. c. samples to be sure of the cyanide titration. However, there seems no doubt that under certain conditions a small amount of cyanide can be regenerated from the ferrocyanide by the direct current, and this factor is another possible advantage in electrolysis over zinc precipitation.

^a Kern, E. F., work cited, p. 264.

SHEET-IRON ELECTRODES COMPARED WITH IRON WIRE-CLOTH ELECTRODES.

To determine whether the iron wire-cloth electrodes were actually superior to those of sheet iron, 12 sheet-iron anodes were made. These sheets, $3\frac{1}{4}$ inches high by 3 inches wide, were held by two hard rubber strips, one on each side, so extended as to keep the lower edge $\frac{1}{4}$ inch above the bottom of the box. The 12 sheet-iron cathodes were 4 inches high by 3 inches wide, in the clear, and were held in ebonite insulating strips. Four $\frac{1}{4}$ -inch perforations were made near the top of each strip to allow the solution to circulate. The cathodes were coated with a thin film of graphite and vaseline. The electrodes were $\frac{1}{4}$ inch apart. The effective cathode area was 1.25 square feet or about 0.12 square meter. Circulation was produced by the centrifugal pump, and the flow was up and down through the $\frac{1}{4}$ -inch by 3-inch spaces, at the rate of only 0.56 liter per minute in the beginning. The results were as follows:

Results of tests with sheet-iron electrodes.

Time, hours.	Volts.	Amperes.	KC _y in solution, per cent.	Silver per 100 c. c., mg.
0	0	0	0.215	16.75
1	1.5	0.60-0.22	.214	13.99
2	1.5	.27	.214	12.05
3	1.5	.265	.213	10.43
4	1.5	.23	.212	9.13
5	1.5	.24	.210	8.65
6	1.5	.21	.209	8.25
7	1.5	.20	.209	6.86

The results (see fig. 20) at the end of the first hour were so poor that during the second hour the cathodes were removed, cleaned with gasoline of the graphite-vaseline mixture and of silver, and then replaced. At the end of the fourth hour the electrodes were placed parallel with the longer dimension of the box to increase the velocity of flow to 6 liters per minute. The experiment was repeated with many variations without graphite and vaseline, in which a voltage of 2 volts and a current of 1 ampere were employed, and also 2.5 volts and 3 amperes. With the stronger current the precipitation was very little better. At 0.95 ampere small bubbles of gas filled the solution and this gas increased with higher current densities. The advantage of the greater surface presented by the wire-cloth cathodes compared with that of the sheet-iron cathodes was evident.

COMPARISON OF SILVER CLEAN-UP FROM SHEET-IRON ANODE WITH CLEAN-UP FROM WIRE-GAUZE ANODES.

The clean-up box that was used held 500 c. c. of solution; the solution contained 0.1 per cent KC_y. The voltage was not recorded;

from memory I judge that it was derived from one Daniell cell and was higher at the end than in the beginning. The anode was of sheet iron 8.3 by 8.7 cm. in size, giving an area of 144.2 square centimeters for the two sides. The current was 0.1 ampere at first, finally becoming 0.005 ampere. The sheets of silver that finally

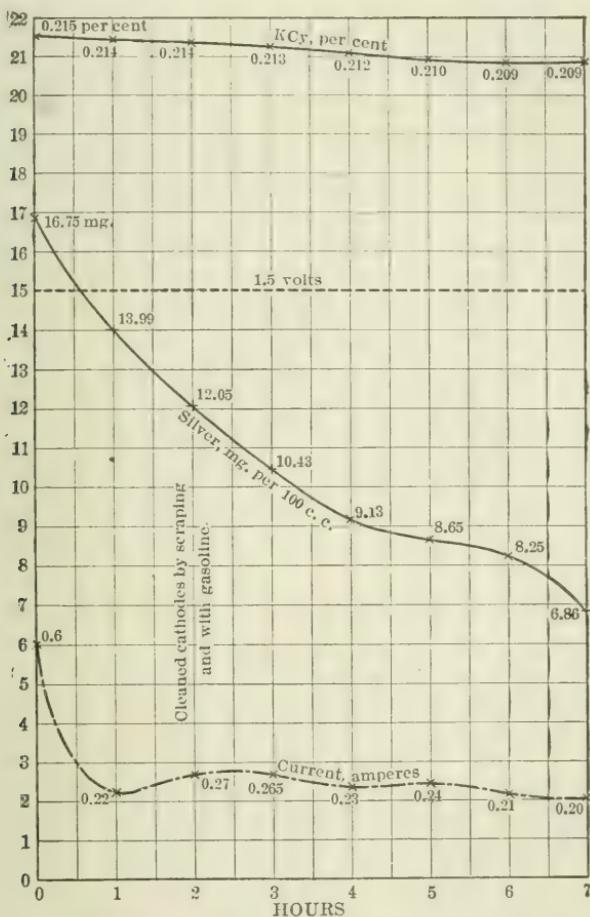


FIGURE 20.—Electrodeposition results with sheet-iron electrodes. Twelve anodes, effective area 1.25 square feet, and 12 cathodes, effective area 1.25 square feet, spaced $\frac{1}{4}$ inch. Silver cyanide solution, rate of flow 0.56 to 6 liters per minute. During first four hours, electrodes vertical, velocity of flow up and down slots averaged 0.68 inch per minute. After fourth hour, electrodes parallel with flow, velocity much increased. Figure 16 (p. 66), compared with this figure, shows advantage of using wire-cloth cathodes and larger area of cathode than of anode.

were peeled off were about 0.23 mm. thick; one weighed 19.78 grams and the other 16.85 grams. To the total weight of the sheet silver recovered, 36.63 grams, should be added that of the silver slimes from solution (0.39 gram), making a total of 37.02 grams. The residual cyanide solution, which was a deep yellow, contained

0.065 per cent free cyanide and 0.153 gram iron per liter. Half of this weight of iron had dissolved from the anode.

Another clean-up was made during which the stripping solution was made to circulate through the clean-up box. The cathode used was $2\frac{1}{4}$ by $3\frac{1}{2}$ inches in size, giving an area for the two sides of 19.26 square inches or 0.134 square foot. With 10 wire-cloth wire cathodes in two bunches of five, connected as anodes on each side of the cathode, 1 Daniell cell gave 0.25 ampere. When the solution was strongly circulating, the current rose to 0.35; on the circulation being stopped, the amperage fell in one minute to 0.1 and the voltage rose to 0.7. Finally the current fell to 0.2 ampere, and the cyanide content to 0.25 per cent; and the solution contained 29.73 mg. of silver per 100 c. c. The solution was now strengthened to 0.45 per cent free KCy and the voltage was raised to 1.25, when the last two bunches of five cathodes from the deposition box were put in.

The current density was at first 2.61 and finally 0.373 ampere per square foot. This density was too high except when the rate of circulation of the solution also was high. About 50 mg. of fine silver dust came off in washing, and only 10 mg. were found in the clean-up box. The final solution contained 0.41 per cent KCy and 3.55 mg. of silver per 100 c. c. The cathodes were apparently stripped clean. The amount of silver recovered from the cathodes was as follows:

Quantity of silver recovered from cathodes.

	Grams.
From 1st set (4×5) of cathodes	7.700
From 2nd set (4×5) of cathodes	5.977
From 3rd set (2×10) of cathodes	2.258
 Total recovery	 15.935

The solution treated in the deposition box contained 15.040 grams of silver, giving an excess recovered of 0.895 gram, which came from the original cathodes that were not entirely cleaned in the previous test. The silver recovered was entirely free from gold, copper, or iron, and was decidedly fine. The silver dissolved in nitric acid, leaving no residue, and the nitric acid solution gave no color test with ammonia.

THE USE OF THE CLEAN-UP BOX WITH RAPID CIRCULATION.

The capacity of the deposition box had now been so increased that it far exceeded that of the clean-up box, and I next tried to increase the capacity of the latter in the way that I had that of the deposition box. This was not easy, as it was desirable to use sheet cathodes from which the metal could be stripped.

The sheet-iron cathodes of the clean-up box were of two types, which will be designated as A and B. The surface of the type-A

cathodes exposed to the solution was 7.5 by 8.5 cm. These cathodes touched the bottom of the box, and were perforated near the top with four 6-mm. holes to allow the solution to pass through. The total submerged area of the six type-A cathodes was 765 square centimeters. The six type-B cathodes used were each 7.5 by 8 cm. in size. They were so placed that they did not quite touch the bottom of the box, in order to force the solution to pass under. The area of these six cathodes on both sides was 720 square centimeters. The total cathode area was thus 1,485 square centimeters, or a little less than one-sixth square meter, or about 1.5 square feet.

The vertical edges of the cathodes A and B were insulated by ebonite strips 1 cm. wide and 6 mm. thick, which were placed on each side of the plates to stiffen them and to prevent their touching the electrodes to be stripped. The plates were then rubbed with a mixture of graphite and vaseline, just enough vaseline being used to make the graphite adhere. This coating was rubbed to a dry finish and the cathodes A and B were placed in alternate positions to force a proper circulation of the solution. Between the 12 cathodes were placed the wire-cloth anodes to be stripped, which had been the cathodes of the deposition box. Thirteen to 26 of these could be stripped at a time. In the first experiment 14 were used. The solution was circulated rapidly through the box by a small centrifugal pump.

The 14 wire cathodes in bunches of five, to be stripped, had been used before and had an unknown quantity of silver deposited on them. In the present test four different lots of dilute cyanide solutions, containing silver, were deposited on them in the usual way. The depositions were continued at convenient intervals for several days, the cathodes being taken out and dried between times. The conditions of deposition were unfavorable to good precipitation, on account of the local action between the iron and the silver during the drying, which would not occur in continuous practice. In all 55.328 grams of silver was calculated to have been deposited on the cathodes in these four runs, the exact amount, however, being greater on account of the unknown amount on them in the beginning.

Stripping followed with one small "Nungesser" cell (zinc and copper oxide in NaHO) which gave a voltage of 0.75 in open circuit, but much less on a closed circuit. At first, with 12 cathodes and 14 anodes to be stripped, the cell gave 0.4 volt and 1.4 amperes on a closed circuit. This soon fell to 0.3 volt, but the current remained at slightly more than 1 ampere till the electrodes were nearly stripped (five hours), when the voltage rose to 0.58 and the amperage fell to 0.38. In seven and one-half hours the wire electrodes were apparently completely stripped, the voltage of the cell having risen

to 0.68 volt and the current having fallen to 0.2 ampere, the current density being 8.0 amperes per square meter at the start and about 1.11 at the end of the stripping. The silver formed a brilliant white deposit and adhered firmly. The only trouble was a tendency for the silver to creep on the edges of the ebonite strips where a little graphite had accidentally adhered.

The stripped anodes were then removed, washed, and dried, and the process of electroconcentration was again undertaken. The six type-A electrodes were now made anodes, and the B electrodes were made the cathodes. The voltage was varied from 0.2 volt at the start to 0.68 at the end. The current at the start was 0.96 ampere and at the end 0.062. The cell was run 22 hours, when the silver was found to be entirely removed and concentrated on the six B cathodes. It was found to be in beautiful coherent sheets that could be readily peeled off. The formation of these strips is a complete refutation of the statements of Prof. Neumann that this is impossible. The total weight of silver concentrated on the six B cathodes weighed 91.8 grams. The cyanide solution at first contained about 1 per cent KCy. To this more was added from time to time, and at the end of the test the content of free KCy was 0.41 per cent. The silver content at the end was 4.42 grams of silver in 1.25 liters of solution, or about 0.354 per cent. Of course it would have been easily possible to reduce this amount of residual silver to almost any smaller amount by electrolysis. In one test the silver content of the solution in the stripping box was reduced to 0.98 mg. per 100 c. c., the KCy content being 0.59 per cent. If the solution were to be discarded the silver value could be reduced to a few cents per ton by circulating the solution a few times through the deposition box.

These excellent results were repeatedly duplicated, and the good coating with this dense current would have been impossible without the rapid circulation of the stripping solution.

DEPOSITION OF GOLD ON IRON WIRE-CLOTH CATHODES.

The electrodeposition of gold from cyanide solution is both theoretically and practically more difficult than that of silver. Theoretically the difference is to be judged by the electromotive force determinations of these metals in cyanide solutions.^a Thus in 6.5 per cent KCy solution gold is electropositive to silver by 0.100 volt; in 0.65 per cent KCy solution, by 0.07 volt; in 0.065 per cent KCy solution, by 0.035 volt; and in 0.0065 per cent KCy, by 0.030 volt. This latter strength of solution is near the critical point at which both gold and silver become electronegative to cyanide solutions. Beyond

^a See Christy, S. B., electromotive force of metals in cyanide solutions: Trans. Am. Inst. Min. Eng., vol. 30, 1900, pp. 921-2.

that point, while both metals remain electronegative, the silver becomes less so (less "noble") than does gold.

Practically the extent of the difference by which gold is less easily precipitated from cyanide solutions than is silver increases more than the figures would indicate. This is shown by a study of the following experiment.

DEPOSITION OF GOLD FROM GOLD CYANIDE SOLUTION.

At the beginning of the test there was 22 liters of gold cyanide solution, containing 0.198 per cent KCy, 0.1 per cent KHO, and 3.696 grams Au as KAuCy_2 . Fourteen bunches of five iron-wire cathodes were used. The flow was at the rate of 8 liters per minute, or 480 liters per hour. The mean area was 4 square feet. The results are shown below.

Results of electrodeposition experiment with gold cyanide solution.

Hours.	Volts.	Amperes.	KCy. per cent.	Gold, mg. per 100 c. c.
0	0	0	0.198	16.80
1	1.5	2.00 to 0.6	.190	14.59
2	1.5	0.61 to 0.52	.191 (?)	5.92
3 ^a	1.5	0.52 to 30	.188	1.40
4	1.5	1.02 to 0.43	.182	.09
5	1.5	0.41	.174	.02
6	1.5	0.41	.165	Trace.

^a Note interruption of current for half an hour. Here the electric current failed, cathodes were removed and drained. After delay of one-half hour the current came on and the cathodes were replaced. The current was high at first, then dropped rapidly.

The ampere-hour efficiency, assuming gold as univalent, 7.35 grams per ampere-hours, was as follows:

Data showing ampere-hour efficiency.

Hour.	Gold, mg. per liter.		Liters treated.	Gold pre- cipitated, grams.	Average ampere- hours.	Theoretical gold, grams.	Ampere- hour efficiency.
	In sample.	Difference.					
0	168.0						
1	145.9	22.1	21.79	0.4816	1.12	8.2320	5.79
2	59.2	86.7	21.68	1.8800	.57	4.1897	44.87
3	14.0	45.2	21.57	.9750	.46	3.3812	28.71
4	.9	13.1	21.46	.2811	.56	4.1162	6.83
5	.2	.7	21.35	.0149	.41	3.0137	.49
6	Trace.	.2	21.24	.0042	.41	3.0137	.0139
				3.6368		25.9465	14.01

In the above experiment, the initial volume, 22 liters, was reduced by 0.210 liter for the first sample and by 0.110 liter for each succeeding sample, taken at the end of each hour. Hence a deduction from the volume for the solution treated each hour is necessary. A num-

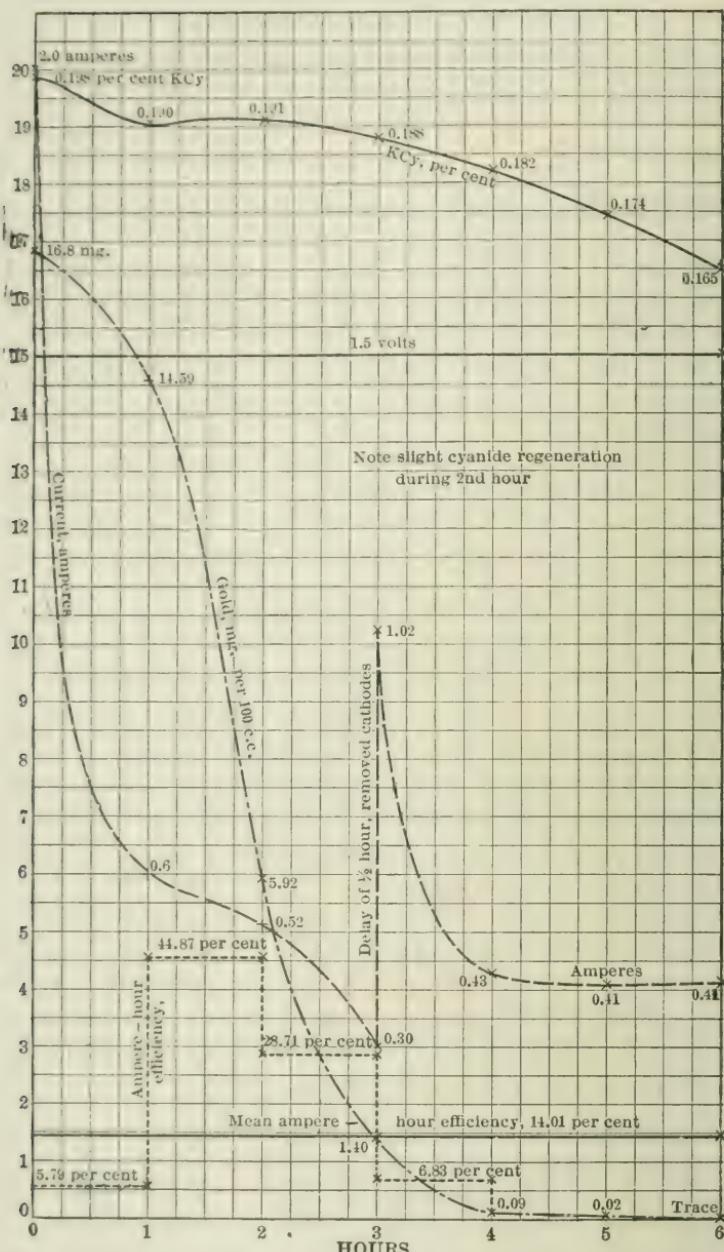


FIGURE 21.—Electrodeposition results with gold cyanide solution. Twenty-two liters of solution, containing 0.198 per cent KCy, 0.1 per cent KIO₃, and 3.696 grams of Au as KAuC₈, taken for test. Seventy 16-mesh wire-cloth cathodes; estimated area, both sides, 2 to 10 square feet. Rate of flow, 8 liters per minute; velocity through open box, 46 inches per minute; through cathodes, 105 inches. Note slight cyanide regeneration during second hour.

ber of important conclusions may be drawn from this experiment (see fig. 21).

First, note the low efficiency during the first hour. The cause of this low efficiency is that between the experiments, which were dis-

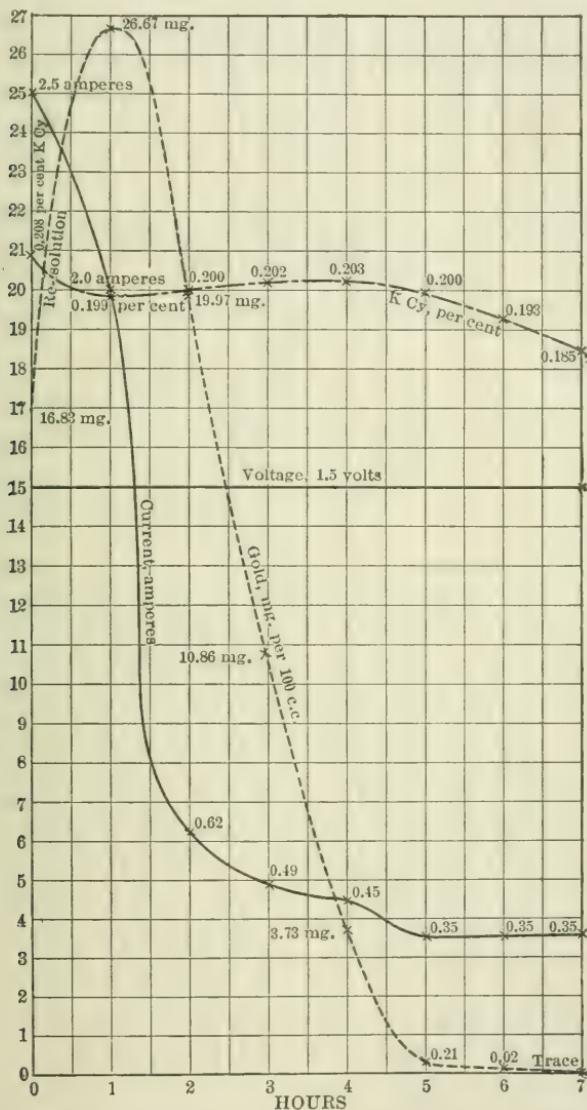


FIGURE 22.—Gold deposition results showing effect of local action on iron-wire cathodes. Eight carbon comb anodes; 70 16-mesh cathodes; estimated surface, between 2 and 10 square feet. Twenty-two liters of solution, containing 0.208 per cent KCy, and 16.83 mg. Au per 100 c. c. Rate of flow, 8 liters per minute; velocity, 46 inches per minute through open box and 105 through cathodes.

continuous, the iron-wire cathodes had rusted, and a large part of the current in the first hour was consumed in reducing the oxide. The

serious nature of this trouble is shown more clearly in later experiments.

Second, the high ampere-hour efficiency in the second hour (44.87 per cent) would have been still higher if the cathodes had been entirely clean the first hour. The ampere-hour efficiency for the entire six hours, 14.01 per cent, was remarkably high.

The extraction was good. In five hours the gold value of the solution was reduced to 12 cents per ton and in six hours to less than 6 cents. The precipitation is, however, much less rapid than with silver. The rate would have been increased by a higher voltage but at the cost of the ampere-hour efficiency.

A slight regeneration of cyanide during the second hour, when the gold precipitation was greatest, was noted.

THE EFFECT OF LOCAL ACTION ON IRON-WIRE CATHODES.

Attention has already been called to the local action that takes place in intermittent silver precipitation. With gold it is more marked. The serious nature of this difficulty is illustrated by the following experiment: The gold-coated cathodes were drained and allowed to dry over night. They were not dried by heat, as the unequal expansion of gold and iron might cause the coat to scale. However, local action resulted which oxidized the iron with disastrous results. For the first hour, gold dissolved in spite of the current, showing that the coating of gold had been undercut by the rust, thus insulating it from the iron cathode, and allowing it to dissolve. The second hour still shows the bad effect of the rust, although the deposition was fair. The details and results of the experiment (see fig. 22) which illustrates this are as follows:

There were employed eight new carbon anodes. The cathodes were the 14 bunches of fine 16-mesh wire-gauze screens, which had been partly coated with gold from the previous run. The total volume of the solution at the start was 22 liters; it contained 0.208 per cent KCy, 168.3 milligrams gold per liter, and 0.1 per cent KHO. The flow was 8 liters per minute, or 480 liters per hour. The total cathode area was between 1.57 and 7.85 square feet. The area of the composite wire cathodes is hard to calculate. The minimum area would be that of the section of the cloth, 0.112 square feet (counting both faces) for each of the 14 groups, or 1.57 square feet. The maximum would be 5 times 1.57, or 7.85 square feet. In time the entire cloth becomes covered with metal, but not all at once. The true mean would probably be about 4 square feet, a little below the average of 4.71 square feet. The ampere-hour efficiency in this experiment is shown in the following table:

Data showing ampere-hour efficiency in experiment.

Hour.	Gold, mg. per liter.	Difference.	Number of liters treated.	Gold precipitation, grams.	Average ampere-hours.	Theoretical gold, grams.	Ampere-hour efficiency, per cent.
0	168.3						
1	266.7	-98.4	21.79	-2.1442	2.100	15.434	Negative.
2	199.7	+67.0	21.68	+1.4525	1.570	11.540	12.58
3	108.6	+91.1	21.57	+1.9650	.526	3.866	50.81
4	37.3	+71.3	21.46	+1.5300	.478	3.513	43.55
5	2.1	+35.2	21.35	+ .7515	.406	2.984	25.18
6	.2	+ 1.9	21.24	+ .0404	.350	2.572	1.57
7	Trace.	+ .2	21.13	+ .0042	.350	2.572	.16
				+3.5994		42.481	

During the first hour the ampere-hour efficiency was negative, as nearly two-thirds of the gold already precipitated was redissolved; but in the next hour the current had begun to cure the evil, and 12.58 per cent of the current was utilized. During the next hour the efficiency had risen to 50.81 per cent, slowly falling to a fraction of 1 per cent. Besides the dissolved gold the new gold, amounting to 3.6842 grams, was practically all precipitated. However, considering the net gold only, the efficiency is high. Dividing 3.5994 by 42.481 (the weight of gold that the current should have precipitated) gives for the whole period 8.47 per cent, which is a good result in spite of the poor start.

To be sure that the carbon anodes had not prevented the solution (containing 0.185 per cent KCy) from dissolving gold, 100 c. c. of the tailing solution was rotated for half an hour in a $\frac{1}{2}$ -liter flask filled with air to aerate it, and then was rotated with a gold strip in it for one hour. The quantity of gold thus dissolved was 2.47 mg. A parallel experiment with pure KCy (0.185 per cent) solution gave 2.41 mg. Hence the carbon anodes had not prevented solution of gold.

The same wire-cloth cathodes, 14 groups of five, from the above test with gold still on them were again treated with practically the same results. (See figure 23). Eight of the hard-carbon anodes were used. The cathode area was between 1.57 and 7.85 square feet. The rate of flow was 8 liters per minute. The ampere-hour efficiency under the above conditions is shown in the following table:

Data showing ampere-hour efficiency of experiment.

Hour.	Gold, mg. per liter.		Number of liters treated.	Gold precipitated, grams.	Average ampere-hours.	Theoretical gold, grams.	Ampere-hour efficiency, per cent.
	At start.	Difference.					
0	169.3						
1	270.4	-101.1 (?)	21.79	-2.2030 (?)	0.568	4.175	Negative.
2	218.9	+ 51.5	21.68	+1.1165	.410	3.017	37.01
3	165.5	+ 53.4	21.57	+1.1518	.410	3.017	38.18
4	94.0	+ 71.5	21.46	+1.5248	.430	3.161	48.24
5	29.3	+ 64.7	21.35	+1.3812	.434	3.190	43.30
6	2.0	+ 27.3	21.24	+ .5798	.382	2.807	20.66
7	.2	+ 1.8	21.13	+ .0380	.345	2.536	1.50

The net amount of gold precipitated was 3.5891 grams, whereas the current should have precipitated 21.903 grams. Therefore, the total ampere-hour efficiency was 16.39 per cent, and in spite of the poor

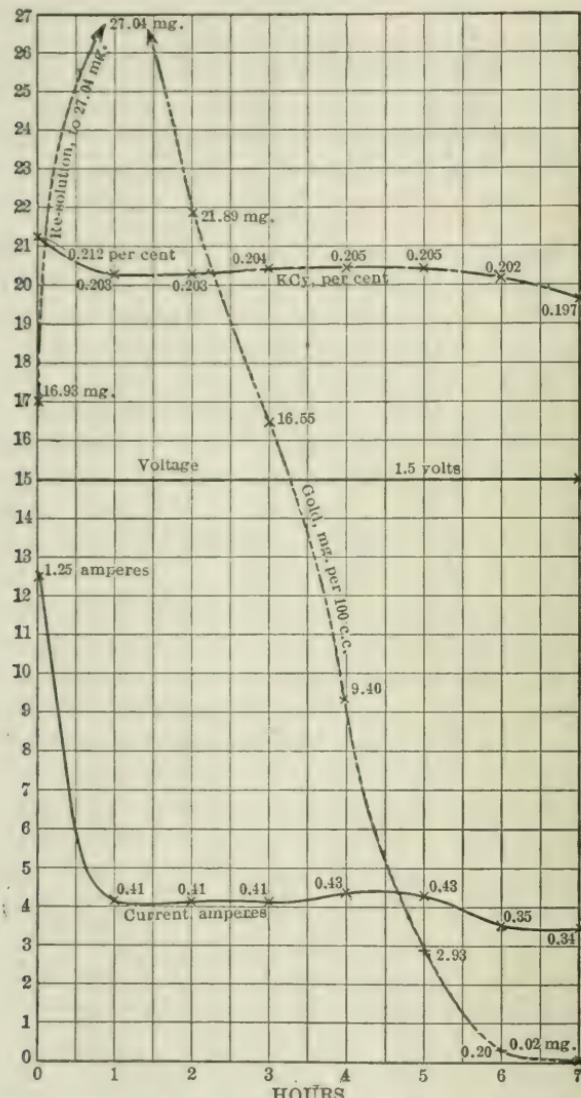


FIGURE 23.—Electrodeposition results showing re-solution of gold due to rusting of cathodes. Eight "Electra" carbon comb anodes. Seventy 16-mesh wire-gauze cathodes, in 14 groups of 5 each; estimated total surface area, between 2 and 10 square feet. Solution, 22 liters, contained 0.212 per cent KCy, 0.1 per cent KHO, and 16.93 mg. Au per 100 c. c. Rate of flow, 8 liters per minute; velocity through open box, 46 inches per minute; through cathodes, 105. Note fall of cyanide during solution of gold and slight rise during fall of gold.

start was decidedly satisfactory for the whole period. The current was rather low because the solution was a new one used for the first

time, and did not contain so many dissolved salts; the current was relatively better after a while because the contacts were better. The fall of the cyanide during the solution of the gold and the slight rise during its rapid precipitation should be noted. The rise was less than the fall, owing to continuous oxidation.

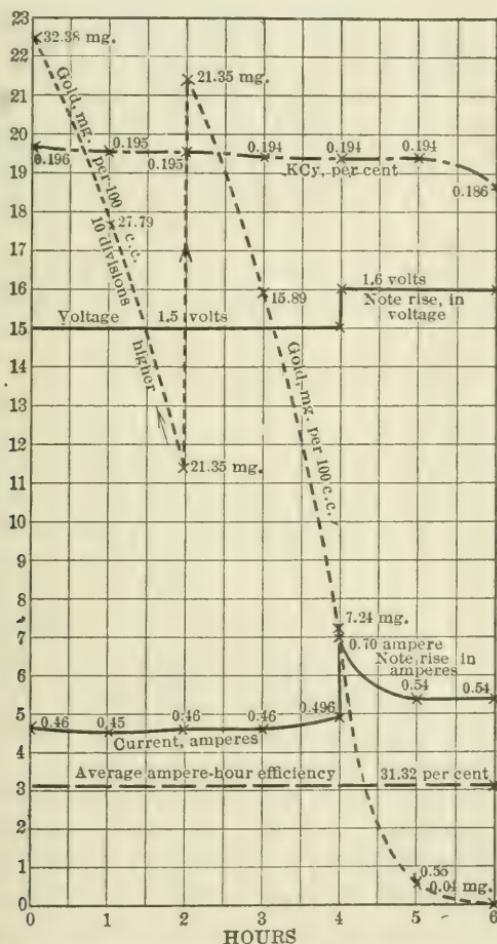


FIGURE 24.—Electrodeposition results with rich gold solution. Solution, 21.68 liters, containing 32.48 mg. Au per 100 c. c. Six carbon comb anodes; seventy (14 groups of 5) 16-mesh wire-cloth cathodes; total estimated surface area, between 2 and 10 square feet. Rate of flow, 8 liters per minute or 480 per hour; velocity through open box, 46 inches per minute; through cathodes, 105.

The next experiment was made with 14 bunches of five cathodes of 16-mesh wire cloth. The total area of these was estimated to be between 1.57 to 7.85 square feet. They were gold coated from previous use. Six carbon anodes were used. The solution contained 0.205 per cent KCy and 0.1 per cent KHO. The flow was 8 liters per minute. The solution at the start contained 16.92 mg. gold per liter,

but owing to bad contacts, the gold dissolved, so that the content in the solution increased to 32.38 mg. The ampere-hour efficiency under these conditions (see also fig. 24) is shown in the following table:

Data showing ampere-hour efficiency in experiment.

Hour.	Gold, mg. per liter.		Number of liters treated.	Gold precipitated, grams.	Average ampere-hours.	Theoretical gold, grams.	Ampere-hour efficiency, per cent.
	At start.	Difference.					
0	323.8		21.68	0.9951	0.45	3.307	30.09
1	277.9	45.9	21.57	1.3890	.46	3.382	41.07
2	213.5	64.4	21.46	1.1717	.46	3.382	34.65
3	158.9	54.6	21.35	1.8467	.496	3.645	50.63
4	72.4	86.5	21.24	1.4209	.605	4.447	31.95
5	5.5	66.9	21.13	0.1078	.540	3.969	2.72
6	0.4	5.1					

The average efficiency for the whole period is thus shown to be 31.32 per cent, a result which certainly is very satisfactory.

DEPOSITION OF GOLD FROM DILUTE SOLUTION ON RUSTED IRON CATHODES.

The solution consisted of approximately 22 liters of 0.047 per cent cyanide, containing 1.010 mg. of gold per 100 c. c. Seventy (14 sets of five) coarse wire cathodes were used, the area being between 1.57 and 7.85 square feet. The rate of flow was 7 liters per minute, or 420 liters per hour. The results of this experiment are graphically shown in figure 25.

The cathodes had been used before and had rusted, with an unknown amount of gold on them. During the first hour, owing to the extent of the rusting, the gold stripped off the cathodes and the content in the solution increased to 2.46 mg. per 100 c. c. As stripping would not occur in continuous practice, the analysis begins with this content of gold in the solution. At the close of the experiment all the cathodes except two were coated with gold, but the coating was irregular, showing the effect of the rust. Near the surface, where air had access, the coating was thinner than below. The carbon anode at 1.6 volts did not show any signs of corrosion. The ampere-hour efficiency attained in this experiment is as follows:

Data showing ampere-hour efficiency attained.

Hour.	Gold, grams per liter.		Number of liters treated.	Gold precipitated, grams.	Average ampere-hours.	Theoretical gold, grams.	Ampere-hour efficiency, per cent.
	At Start.	Difference.					
0	0.0246		21.68	0.0260	0.52	3.824	0.68
1	.0234	.0012	21.57	.0518	.46	3.381	1.53
2	.0210	.0024	21.46	.2900	.36	2.646	10.96
3	.0075	.0135	21.35	.0512	.34	2.499	2.05
4	.0051	.0024	21.24	.0595	.32	2.352	2.53
5	.0023	.0028					

This table shows the detrimental effect of rust on iron-wire cathodes. The gold that had been previously deposited on the cathodes dissolved in spite of the current. It is possible that oxide of iron had formed under the gold and insulated it from the iron, thus enabling the gold to redissolve. The detrimental effect of the rust continued during the next hour and the ampere-hour efficiency was only 0.68 per cent. In the next hour it had risen to 1.53 per cent, and in the next hour to 10.96 per cent. The current, then, is capable of curing the evil, and for this purpose I have devised what I call the "hospital cell," mentioned on page 113.

A test which further shows the effect of rust upon cathodes is the following: Seventy (14 sets of five) gold-coated rusted iron-wire cathodes were used in a solution containing about 1 mg. gold per 100 c. c., or \$6.03 a ton. The cathode surface was between 1.57 and 7.85 square feet. The flow was 7 liters per minute. The experiment was begun with six perforated platinum anodes. The pressure was 2.5 volts. The current at first was 1.33 amperes, falling in four hours to 0.91 ampere. The gold on the rusted iron wires dissolved in spite of the current. The solution was then made up to 22 liters, when it contained 4.12 mg. gold per 100 c. c. and 0.42 per cent KCy. When six perforated and peroxidized-lead anodes were used the voltage re-

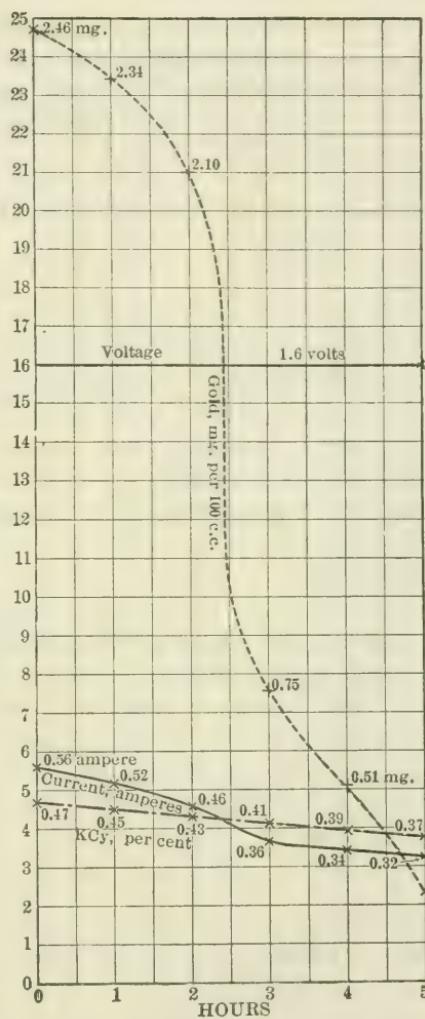


FIGURE 25.—Electrodeposition results with dilute gold solution on rusted iron-wire cathodes. Solution, 21.08 liters, contained 0.047 per cent KCy, 0.1 per cent KHO, and 2.46 mg. Au per 100 c. c. Seventy (14 sets of five) 16-mesh wire-cloth cathodes; estimated surface area, between 2 and 10 square feet. Rate of flow, 7 liters per minute, or 420 per hour; velocity through open box, 41 inches per minute; through cathodes, 91. No rise in cyanide was shown.

mained unchanged, but immediately the current rose to 3.65 amperes. The results are graphically shown in figure 26. The current efficiency was as follows:

Data showing ampere-hour efficiency in test.

Hour.	Gold, grams per liter.		Number of liters treated.	Gold precipitated, grams.	Average ampere-hours.	Theoretical gold, grams.	Ampere-hour efficiency, per cent.
	At start.	Difference.					
0	41.2		38.7	22.00	0.85140	3.07	22.563
1	2.5						3.77
2	0.5		2.0	21.89	0.04378	3.59	26.240
3	Trace.		0.5	21.78	0.01089	3.55	26.093

The precipitation is at the rate of about 176 tons per day in a 1-ton box, much better than that obtained by Siemens & Halske. Moreover, this result is evidently all that could be desired, but it was accomplished at the expense of the ampere-hour efficiency. Of course good precipitation is vital, and is more important than electrical efficiency. This would have been higher, except for the rusted condition of the cathodes. The great importance of overcoming the difficulty from rusty cathodes is evident, and will be specially considered later.

Most of these experiments with gold solutions were conducted at too low a voltage for rapid and complete precipitation. Low voltages were purposely used to find the lowest limit that would give high electrical efficiency and satisfactory regeneration of cyanide. With the ordinary gold solutions used in mill practice the cyanide regeneration is so small that it is obviously better to run at a higher voltage, at least 2.5 volts, to insure rapid and complete precipitation.

EXAMPLE OF A GOLD CLEAN-UP.

The next problem for consideration is that of recovering the gold deposited upon the iron wire-cloth cathodes. Fourteen "bunches of five" of these cathodes had been coated with about 14.7 grams of gold in the experiments just described.

Six flat, sheet-iron, graphite-coated cathodes were inserted in the box along with the 14 cathodes to be stripped and now serving as anodes. A 0.97 per cent potassium cyanide solution was circulated in the stripping box by means of the centrifugal pump. A "Nungessor" cell was used to supply the electrolytic current. The voltage, which at first was 0.75 volt, decreased in one hour to 0.39, then, as the stripping progressed, gradually rose to 0.69 in six hours. The gold was thus concentrated on both sides of six sheet-iron cathodes. As the film was very thin, however, three of the cathodes were made anodes and the gold was all concentrated on three cathodes.

The Nungessor cell gave at first 0.50 volt and 0.26 ampere. After

being allowed to run 16 hours over night, the cell gave in the morning a voltage of 0.70, and the current had fallen to 0.001 ampere. The three cathodes were coated on both sides with a beautiful clear yellow coat of metallic gold which could be easily stripped from the graphite-coated iron in a tough coherent film, the gold thus recovered weighing 6.069 grams. The cyanide content was reduced to 0.57 per cent during this deposition.

The solution from the clean-up box contained 329.05 mg. gold per 100 c. c. (one-third per cent), thus the 1,800 c. c. held 5.923 grams. Loosely adhering to the cathodes was some fine gold which weighed 130 mg. Hence there was recovered in sheet metal, by a voltage of less than one volt, 6.069 grams of sheet gold and 0.130 gram of scrap. The amount of gold in solution not precipitated was 5.923 grams, making a total weight of 12.122 grams. Unfortunately in starting the experiment part of the rich solution was lost so that a check was not possible.

Evidently, to recover all the gold a higher voltage, say 1.6 or 2.5 volts, would have been necessary. Complete precipitation and recovery of the gold by electrolysis could be made at any time. This has been done time and time again,

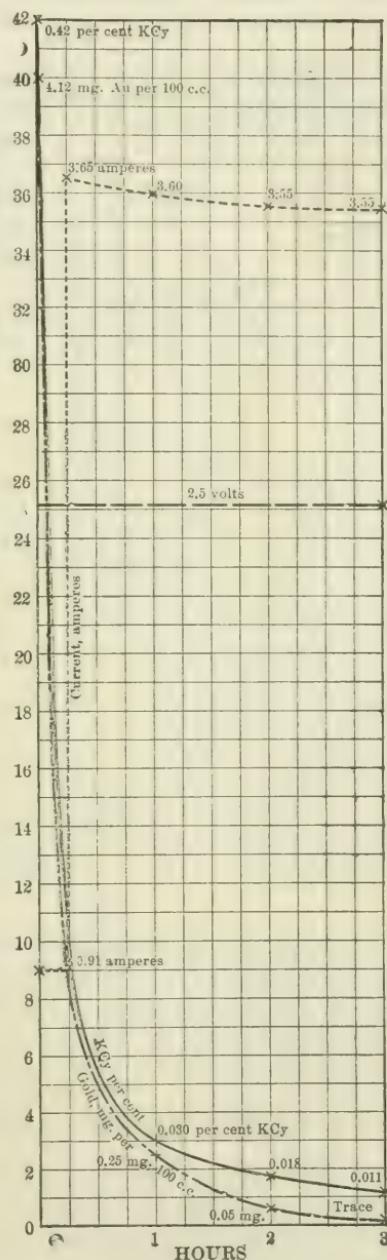


FIGURE 26.—Electrodeposition results showing effect of rust on cathodes. Serventy (14 sets of five) 16-mesh gold-coated rusted wire-cloth cathodes used; estimated surface area, between 2 and 10 square feet. Solution, 22 liters, contained 0.42 per cent KO₄, 0.1 per cent K₂IO₃, and 4.12 mg. Au per 100 c. c. Rate of flow, 7 liters per minute or 420 liters per hour; velocity through open box, 41 inches per minute; through cathodes, 91. For first quarter hour, 6 platinum anodes used; current was only 0.91 ampere; then 6 perforated peroxidized (PbO₂) lead anodes were used; current rose to 3.65 amperes. Note the better precipitation at higher current, but greater and continuous destruction of cyanide.

so there is no doubt on that point. The sheets of gold adhering to the cathodes obtained here are a complete refutation of the claim of Prof. Neumann that recovery of the gold in this manner is impossible.

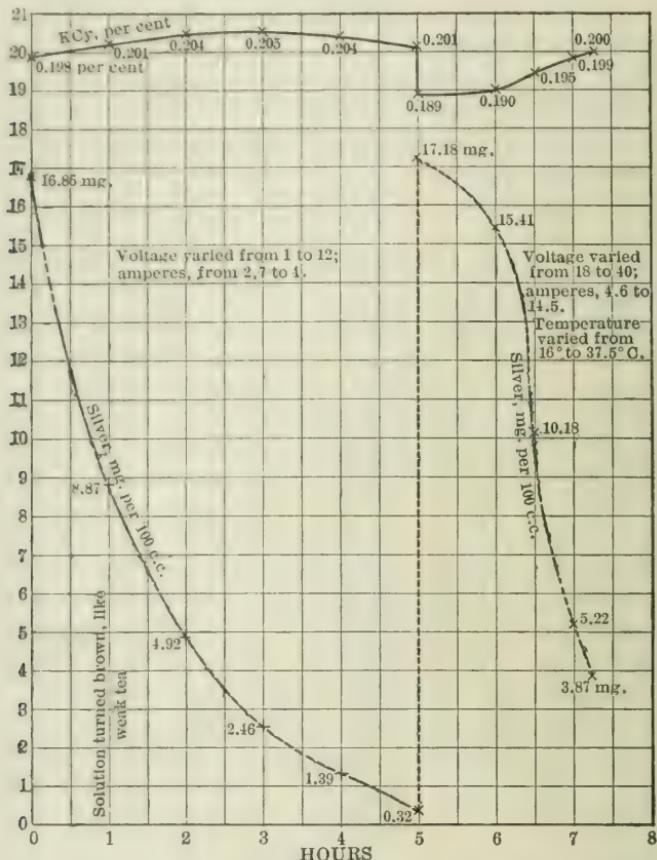


FIGURE 27.—Results of silver electrodeposition with cathodes and anodes horizontal. One perforated sheet-iron anode. One set of five 30-mesh iron wire-cloth cathodes, each 10 by 8.5 cm.; total area of pervious part, 81 square cm.; area when covered with silver was indeterminate. Rate of flow, 11 liters per minute or 660 per hour; velocity through open box, 53 inches per minute; through cathodes, 120.

RECOVERY OF SILVER ON HORIZONTAL PERVERIOUS CATHODES.

All the electrodes previously considered were placed vertically in the deposition box. It was now thought wise to see what could be done in silver recovery by using horizontal pervious cathodes, with removable pervious anodes above them. If this arrangement were successful, a clean-up would be unnecessary, for the silver could be scooped up with a shovel. Such a construction is not so favorable for deposition as the previous arrangement, for only one anode

and one cathode can be used in each box. An anode can not be placed below the cathode on account of interruptions from the gas set free; the area could be increased, however, by placing the shallow cells in cascade one above another. High voltages were used in an

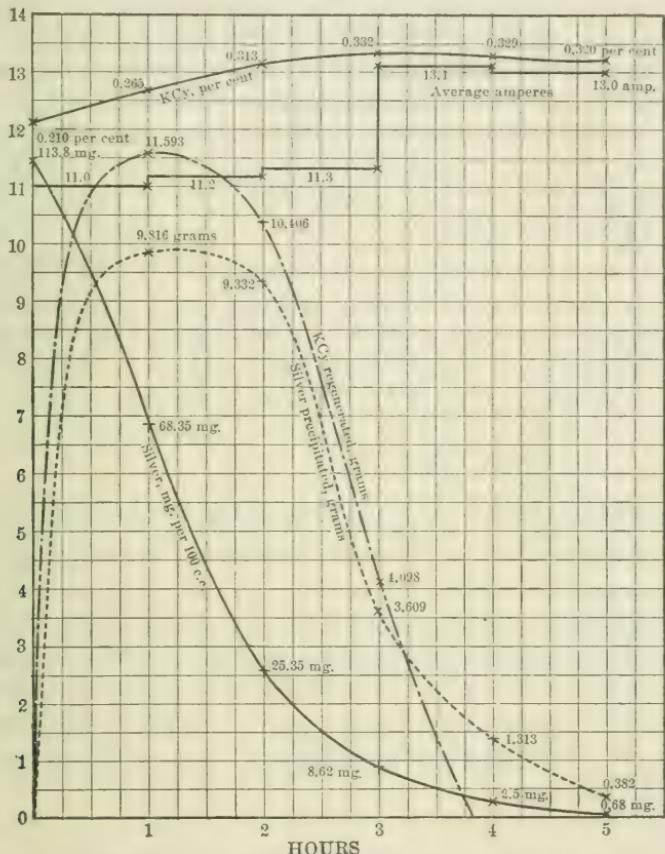


FIGURE 28.—Results of silver electrodeposition with single horizontal electrolytic filter. First 3 hours a perforated platinum plate was used as anode; last 2 hours, 12 turns of No. 18 platinum wire. One set of five 30-mesh iron wire-cloth cathodes, each 10 by 8.5 cm. Rate of flow, 10 to 12 liters per minute; velocity through open box, 53 inches per minute; through cathodes, 120. Voltage, 22 to 50 volts; current, 4.8 to 13.1 amperes, too variable to plot. Room temperature, 16.5° C.; solution rose to 51.5° C. in 5 hours. Note parallelism between weight of silver deposited and weight of cyanide regenerated.

endeavor to make up for the small cathode surface. Very little silver was deposited on the lower wires of the cathode, the up-growing deposit of silver soon formed its own pervious cathode.

I used only one bunch of five sheets of iron-wire cloth placed horizontally, to serve as the cathode, and a perforated platinum sheet as the anode. The solution was circulated by a centrifugal pump so that it passed continuously down through the anode and then through the

cathode. The cathode was 10 by 8.5 cm. in size, only 81 sq. cm. of which was pervious. The voltage, which varied, began at about 3 and finally was raised to 40 volts. The rate of flow was 11 liters per minute, or 660 liters per hour. The results are shown in figure 27. At the end of the second hour the solution began to have a slight brownish cast, which gradually increased, till at last it was dark, reddish brown, about like black-tea infusion. Its temperature had risen to 37.5° C. The room temperature was 20° C. At the end of the fifth hour 3.76 grams of Ag as $KAgCy_2$ was added and 1.3 liters of water to make the total volume up to 22 liters. The silver was deposited as a loose, gray sponge on the wire gauze, which was coated only on the top.

Even if boxes were separately arranged in cascade one over another, it is probable that sufficient cathode area to render the method practicable could not be obtained. Such high voltages as were used are, of course, out of the question, but the clean-up would be simple (the sponge was a beautiful, feltlike network, pervious to the solution). All that would be necessary in practice would be to remove the silver with a shovel.

EXPERIMENT WITH A HORIZONTAL ELECTROLYTIC FILTER.

An experiment was made with a horizontal electrolytic filter. In this apparatus the anode, of perforated platinum, was at the top. After three hours, 12 turns of No. 18 platinum wire were used. The cathodes were of wire cloth such as had been used previously, and were each 10 by 8.5 cm. in dimension. The solution, 22 liters, contained 0.211 per cent KCy and 0.1 per cent KHO . The flow was at the rate of 10 to 12 liters per minute. The results are shown in figure 28.

At the end of the second hour the experiment was temporarily stopped, and the cathodes were removed during the noon hour at that time. At the end of the third hour the perforated platinum sheet was removed and replaced with a platinum wire anode. This wire anode allowed a better escape of the gas from the anode and gave a stronger current at a lower voltage. The ampere-hour efficiency is shown in the following table:

Data showing ampere-hour efficiency in experiment with horizontal filter.

Hour.	Silver content, mg. per liter.		Number of liters treated.	Silver pre- cipitated, grams.	Ampere- hours.	Theoretical silver, grams.	Ampere- hour efficiency.
	At start.	Difference.					
0	1138.4						
1	683.5	454.9	21.79	9.816	11.0	44.270	22.17
2	253.5	430.0	21.68	9.332	11.2	45.080	20.70
3	86.2	167.3	21.57	3.609	11.3	45.480	7.94
4	25.0	61.2	21.46	1.313	13.1	52.724	2.47
5	6.8	18.2	21.35	0.382	13.0	52.324	0.73

The ampere-hour efficiency was high notwithstanding the wastefully high voltage used; it averaged 10.19 per cent for the entire period. Such high efficiency would have been impossible except for the rapid circulation. The metal came down as a beautiful white, porous layer of spongy silver, $\frac{1}{4}$ inch thick, of such quality as to permit it to be scooped up with a shovel. This might be a convenient modification of the clean-up box, but some material for the "cathode-anodes" would have to be used that would not be corroded after the current were stopped—excelsior charcoal, for instance.

REGENERATION OF CYANIDE.

During the first three hours there was a remarkable regeneration of cyanide, as is shown in the following table:

Data showing regeneration of cyanide.

Hour.	KCy content.	Increase.	Volume treated.	KCy regenerated.
0.....	Per cent. 0.210	Per cent. +0.055	Liters. 21.79	Grams. +11.593
1.....	.265	+ .048	21.68	+10.406
2.....	.313	+ .019	21.57	+ 4.098
3.....	.332	<i>a</i> — .003	21.46	<i>a</i> — .644
4.....	.329	<i>a</i> — .009	21.35	<i>a</i> — 1.922
5.....	.320			

a Loss.

The total number of grams regenerated in three hours is seen to have been 26.097. The ratio of cyanide regenerated to the silver precipitated was as follows:

First hour.	$\frac{\text{Weight of KCy}}{\text{Weight of Ag.}} = \frac{11.593}{9.816} = 1.181.$
Second hour.	$\frac{10.406}{9.332} = 1.121.$
Third hour.	$\frac{4.098}{3.609} = 1.135.$

Suppose that for each gram-atom of silver precipitated (molecular weight, 108), two gram-molecules of KCy (molecular weight, 130) were regenerated; then for each gram of silver 1.2037 grams of KCy would be regenerated at the cathode. In this experiment conditions were more favorable for reduction at the cathode than for oxidation at the anode, and the highest ratio attained was very nearly, but not quite, the maximum that would have been possible had there been no oxidation at the anode. It would seem, then, either that the great current density at the anode tended to prevent oxidation, or that the lesser density at the cathode favored reduction of the cyanate formed at the anode. Probably both tendencies acted together to produce this favorable result.

ANODES.

“Oh, for an anode!” There is no one who has done much electrolytic work who has not uttered this exclamation from the bottom of his soul.

SOLUBLE ANODES.

The idea of using soluble anodes so as to avail one's self of the solution energy of the soluble anode is at first thought a perfectly natural one, but on working over the field, only two soluble metals are available, zinc and aluminum. Logically, iron may be considered as a soluble anode: but for convenience, anodes of iron are discussed under the heading “Insoluble Anodes” (pp. 98 to 108).

ZINC AND ALUMINUM.

If commercial zinc is used as an anode, the gold and the silver are precipitated on the anode by local action, even more than on the cathode. Hence both anode and cathode have to be cleaned. To prevent local action on the anode, the use of amalgamated zinc plates for anodes has been proposed by Croasdale.^a But unless the anodes are made very thick and heavy and expensive, they become brittle when amalgamated and fall to pieces. The large area necessary in treating dilute gold solutions is hard to obtain. The same objections apply with even greater force to the use of soluble aluminum anodes. Difficulties of ore leaching, caused from the gelatinous hydrate of aluminum, are further complications, and quicksilver rots aluminum plates even more fatally than zinc.

I think it is safe to take the position that if zinc or aluminum are to be used to precipitate gold or silver from cyanide solutions, they should be used alone and without external electricity, as the combination of these metals with applied electric energy does not seem to be a happy one.

INSOLUBLE ANODES.

Insoluble anodes, of course, add no energy to the bath, and offer an increased resistance to the current owing to polarization effects. Nevertheless in treating ore solutions such anodes would be better than soluble ones if they really could be obtained absolutely insoluble and permanent in daily use.

PLATINUM.

Platinum, if it were cheap, would solve most of the problems; but except for experimental work and for certain rare uses its high cost puts it entirely out of the question.

^a Croasdale, Stuart, Electrolytic precipitation of gold from cyanide solutions: Eng. and Min. Jour., Dec. 12, 1896, vol. 62, pp. 557-558.

HARD CARBON.

Hard electric-light carbon serves admirably in cyanide solutions when the voltage is kept below that at which water is decomposed. But this point is so low (1.48 volts) that it is below the voltage necessary to use in practice. At higher voltages the carbon is slowly acted upon, and the solution becomes colored like weak tea. I have found, however, by repeated experiments that even when darkly colored such cyanide solution, when aerated, will dissolve gold as freely as fresh cyanide solution of equal strength. This form of carbon resists the chlorides very well but soon succumbs to alkaline sulphates, which are sure to be present in cyanide solutions after treating sulphide ores and must be reckoned with. I have tried to increase the resistance of this form of carbon by boiling for several days in vaseline or paraffin the anodes made of it, in order to confine corrosive action to the surface, but these efforts have been without success.

ACHESON GRAPHITE.

Graphite anodes, as produced by Acheson, of Niagara Falls, in the electric furnace, are a great improvement on the ordinary hard carbon. The substance is a better conductor than ordinary carbon and is much more resistant, but in practice it, too, fails when used with solutions containing soluble sulphates. As already mentioned in the experience with Acheson graphite anodes in the Oliver process, at the North Star mine, as long as the process was confined to the treatment of solutions coming from sands that contained very little sulphate, the anodes stood up very well, but as soon as solutions coming from the concentrated sulphides were treated, the abundant sulphates soon reached the weak points of the anodes and they disintegrated finally into a soft black mud. This failure was one of the causes that led to the abandonment of the entire process. The ease with which the Acheson graphite can be machined in a lathe and built up into many forms is a great advantage. I have used it in my experiments in the form of "comb anodes." These are made by screwing four $\frac{3}{8}$ -inch graphite rods, so as to project $4\frac{1}{2}$ inches, into the rectangular block or base bar, also of graphite. Such anodes are rather brittle and have to be handled carefully, but if sulphate solutions are avoided they will last for years. There is never any doubt as to the security of the connections. I usually solder a copper wire to a brass ring, which tightly fits around one of the projecting rods; then the anode requires no further attention, except to avoid dropping it. Enough has been said to show that the Acheson graphite anode can not be said to solve the entire problem.

PEROXIDIZED-LEAD ANODES.

The discovery by Andreoli that peroxidized-lead anodes could be used in cyanide solutions has been of great value to the art. It does not seem to be a matter of indifference how these anodes are prepared. It would seem as if those prepared either as is done by Mr. Butters—namely, by scratching the surface with a stiff brush and then making them anodes in a 1 per cent solution of permanganate of potassium for at least one hour, employing a current density of 1 ampere per square foot of anode—or else by making them first for a short time cathodes and then anodes in a caustic potash solution containing peroxide of lead, give better results with cyanides than those peroxidized in sulphuric acid. However, it is not absolutely certain which is the better way, as enough work has not been done on the subject.

Well prepared, these anodes last about a year. Sooner or later they begin to show white, downy, fungus-like growths that form usually in vertical streaks, which extend up and down the plate. If these growths are cleaned away, naked lead is seen to have been exposed to corrosion. "Local action" has started and deep depressions are formed in the plate, which soon disintegrates. Prof. Kerns says that these white formations are composed of the hydrate of lead. That they often contain lead cyanide I have proved by the following experiment.

Some of the white formation was washed by decantation till the washings failed to give any reaction for cyanide of potassium. The residue was then placed in a flask, acidified with sulphuric acid, and air was blown through the mixture and allowed to bubble through a 1 per cent solution of caustic potash. In a short time a distinct reaction was obtainable for cyanide in the alkaline solution.

It would appear that the substance is a varying mixture of hydrate, carbonate, and cyanide of lead. In time such a growth sometimes becomes slightly peroxidized on the surface, but once it has started, eats like a cancer through the plate. Prof. Kearns suggests that the cause of these growths starting is the porosity of the peroxide film. This is most likely; but I have seen growths start on thick coatings where the occurrence of pores was unlikely. Seemingly a frequent cause may be the cracking of the rather brittle oxide when the plastic lead beneath it is bent. The films on these long lead strips may be easily cracked by bending of the sheets as they hang loose in the bath, and particularly by their being handled.

Another possibility is that under certain, but as yet unknown conditions of current density (accidental short circuits, perhaps) and temperature, the anion AuCy_2 or its components AuCy and Cy may act as reducing agents on the PbO_2 , thus exposing naked lead to the

action of the current. A similar reaction was encountered when I once tried to dry out a mixture of PbO_2 and glycerin on the steam bath. The mixture was decomposed with almost explosive violence and abundant minute shots of metallic lead were reduced from the mixture.

The flat shape of the ordinary sheet anode renders it peculiarly sensitive to a rupture of the protecting surface by bending. In order to meet this difficulty I have devised an improved anode (U. S. patent No. 883170, Mar. 31, 1908).

For this purpose I construct a frame of wood, shown in vertical longitudinal section at *A*, and in vertical cross section at *B*, in figure 29. If the wooden frame, *a*, is made large it should be strengthened by horizontal cross bars *b*. Strips of lead wire, *c*, one-eighth to one-fourth of an inch thick, and of cylindrical form are drawn through suitable holes bored in the horizontal bars of the frame, spaced one-half to one inch or more, thus stretching the lead wires, like the wires of a harp, alternately up and down through the frame. The wires are connected on the top by a lead bus bar, *d*, large enough to carry the total electric current, the individual wires being so proportioned as to carry their part of the electric current, which they must do without overheating. I prefer to protect the wood from the solution by painting it with the so-called "P & B" paraffin paint or some other similar substance. The bottoms of the lead wires are kept from touching the bottom of the box by placing them in a groove in the lower horizontal cross bar. Where the wires pass over the lead bus bar at the top they are secured to the bus bar, preferably by the process of lead burning rather than soldering, although soldering may be used if necessary. The end of the bus bar is connected at *e* with a copper wire, which connects with the main bus bar or the conductor introducing the positive current. After the anodes are thus constructed, the lead wires are prepared as follows:

In order to get a clean metallic surface on the outside of the wires free from all insulating substances, I connect the wire with

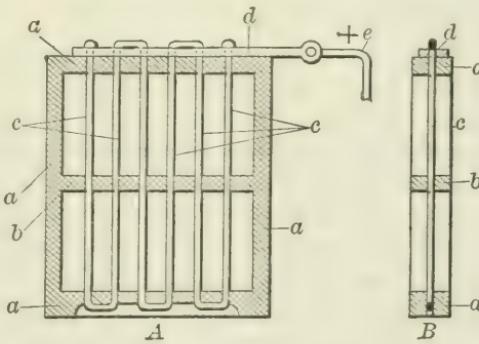


FIGURE 29.—Anode frame designed to prevent bending of metal. *A*, vertical longitudinal section; *B*, vertical cross section. *a*, Wooden frame; *b*, cross bars; *c*, lead wire; *d*, lead bus bar; *e*, copper wire connection to bus bar.

the negative pole of a suitable source of electrical energy, making the lead wires cathodes for a short time in a solution of plumbate of soda. Any oxide or carbonate or hydrate that may have been formed on the outside of the lead wires becomes thus reduced to the metallic state, and an even surface is produced on the outside of the wire of lead. Without waiting for the film to oxidize in any way, the electric current is immediately reversed and the lead wires are made anodes in the same solution and are kept there until a firm, adherent, dark chocolate brown coating of peroxide of lead forms over every portion of the wire exposed to the action of the current. When this coating is of sufficient thickness to protect the wire, it forms a cylindrical film or tube of firmly adherent peroxide of lead. The anodes are then ready to be inserted into the bath of copper sulphate, cyanide of gold or of silver, or other solution to be treated, to act as previous peroxidized-lead anodes. These peroxide-coated lead wires may also be replaced by solid rods of lead peroxide similarly arranged in a suitable frame.

Solid rods of peroxide of lead are not so good conductors as those with a lead core, hence they have to be made larger in section to carry the same current. They are, however, more durable. The wooden frame serves to protect the anode rods both from deformation and from destruction by short circuits. The tube-like coating of PbO_2 upon the lead wires is less likely to scale than the coating on flat moving sheets. With sheets the slightest deformation is likely to cause the coating to scale. The wire anodes thus described expose less surface to the bath than the flat anodes. They thus give a lower oxidizing effect, an advantage which is highly desirable in treating cyanide solutions.

It is hard to obtain data on the conductivity of lead peroxide. Landolt and Börnstein^a give the following for "hydrated lead peroxide":

Conductivity of "hydrated-lead peroxide."

	Conductivity, per c. c.	Resistance, ohms per c. c.
	0.163	6.13 (Shields)
	4.68	0.214 (Weyde)
With 1.5 per cent H_2O -----	335.00	0.00298 (Ferchland)
Pressed powder -----	0.435	2.3 (Sheintz)

The conductivity of lead, at ordinary temperatures is given at 1.99×10^4 to 5.35×10^4 per cubic centimeter, or the resistance varies from 5.02×10^{-5} to 1.87×10^{-5} ohms.

SHEET-IRON ANODES.

As already remarked, logically sheet-iron anodes should be classified under "Soluble anodes," but it is more convenient to discuss

^a Landolt, H. H., Landolt-Börnstein Physikalisch-chemische Tabellen, 3d ed., 1905, p. 723.

them here. Sheet-iron anodes were used first by Siemens. It is well known that with a weak current the iron combines with the cyanide and cyanogen to form potassium ferrocyanide, which forms, with various iron oxides, Prussian blue and other compounds. If the current is of a certain density a protecting oxide coating forms on the anode, from the oxygen set free there, and the anode lasts very well. But if there are chlorides in the solution, the iron salt of this acid forms at the anodes and is secondarily decomposed by the alkaline solution, forming at last hard, warty crusts of ferric hydrate several inches thick. Sulphates seem to be nearly as harmless, but chlorides which are harmless to carbon are fatal to iron anodes.

These crusts increase the electrical resistance. Moreover, they contain considerable cyanide of gold, which has traveled to the anode and become entangled, making an objectionable residue that is hard to treat. Also, the cost of the quantity of iron thus destroyed, amounting in large-scale work to many tons, is considerable.

“ PASSIVE IRON ” ANODES.

The well-known but elusive substance known as “passini iron” was first suggested as an anode in cyanide solutions by Hittorf,^a and it has been again proposed by Kern^b as a cure for the trouble above described. For the purpose he treated the metal as follows:

The iron anodes were rendered passive by first “removing grease by digesting them in hot caustic soda solution, rinsing in water, then putting them into a dilute solution of mixed sulphuric and hydrochloric acids in order to remove all oxide, washing with clean water, thoroughly drying, and finally placing them in concentrated nitric acid and allowing them to remain for about two hours. By this treatment the iron plates were coated with a film of magnetic oxide (Fe_3O_4). On removing the plates from the concentrated nitric acid they were immediately washed with clean water and thoroughly dried to prevent the formation of ferric oxide (Fe_2O_3).” The manner of drying is not mentioned. It is an important omission in such a delicate operation. Kern expresses great satisfaction with the “passive iron anodes,” but the experiments he describes only lasted a couple of hours, and he does not seem to have tried the effect of $NaCl$ and Na_2SO_4 . Long experience shows that the conditions governing “passive iron” are too uncertain and too little understood to pin much faith to anodes so constructed. I have been unable to find any of the many directions for producing them to give a result that would make a permanent anode that would stand up with

^a Hittorf, W., Über passivität der Metalle: Ztschr. Phys. Chemie, Bd. 34, 1900, p. 395.

^b Kern, E. F., Electrolysis of cyanide solutions: Trans. Am. Electrochem. Soc., vol. 24, 1913, pp. 241-270.

cyanide solutions containing chlorides under tensions of three or four volts and not break down. Ferric hydrate and Prussian blue soon form the usual crusts and the anode fails utterly.

If some such method could be perfected it would be of the greatest practical utility, not only in electrolysis, but in all the other industrial uses of iron. The investigation of "passive iron" has occupied the attention of many able men for years, but there is no general agreement as to the cause of the phenomena. I use the plural advisedly. If the cause were once surely settled some practical methods would almost certainly result. But "where doctors disagree who shall decide?" The patient usually succumbs, and that is what happens to the "passive iron" anode when it is put to practical use.

An interesting symposium on the passivity of metals was held November 12, 1913, in London by the Faraday Society.^a The discussion, which is well worth close study, shows that the phenomena are too varied to be covered by a single theory. The three important theories that are held are the following:

1. The oxide film theory, proposed by Faraday.^b

2. The valency theory of Finkelstein and Krüger^c and of Müller.^d This assumes that the metal is in an electric condition which alters its valence and renders it more "noble." Finkelstein assumes that in the case of ordinary iron both bivalent and trivalent atoms are present; that the passivity consists in either removing the bivalent atoms from the surface or changing them into the trivalent kind. Hittorf^e disagrees with Faraday in the assumption, and although he seems to incline to some such view, does not commit himself.

3. The reaction velocity theory of Le Blanc, which presupposes two possible conflicting reactions, the changing rate of which produces the various effects. There are three or four modifications of this theory which are rather metaphysical in their refinements and to discuss them in detail would take us too far afield.

As early as July, 1900, I had hopes of utilizing "passive iron" anodes. Iron was made "passive" in a mixture of strong nitric and sulphuric acids, and after washing the specimens of iron so treated were made anodes in potassium cyanide to which a little silver nitrate had been added. The anodes were attacked with free formation of

^a Senter, G., and others, The passivity of metals: *Trans. Faraday Soc.*, vol. 9, March, 1914, pp. 203-290; abstracted in *Mét. and Chem. Eng.*, vol. 11, December, 1913, p. 679.

^b Faraday, Michael, On a peculiar voltaic condition of iron: *Philos. Mag.*, vol. 9, 1836, pp. 57-65.

^c Finkelstein, Alexls, Über passives Eisen: *Ztschr. Phys. Chemie*, Bd. 39, 1902, pp. 91-110.

^d Müller, W. J., Zur Passivität der Metalle: *Ztschr. Phys. Chemie*, Bd. 48, 1904, pp. 577-584.

^e Hittorf, W., Über die Passivität der Metalle: *Ztschr. Phys. Chemie*, Bd. 34, 1900, p. 393.

hydrates and other compounds. Iron boiled in paraffin was similarly attacked. Electric-light carbon which had been boiled in paraffin to fill the pores was at eight volts disintegrated on the surface into a sludge.

On July 7, 1900, I conducted an experiment with a 0.5 per cent cyanide solution containing gold and silver as cyanides and 1.5 per cent common salt. For the anode I used a small ornamental cast-iron scroll that had been well coated with a magnetic iron coating by the Bower-Barff process. Four volts gave a current of 0.100 ampere, with a wetted area of about 10 square inches. After $3\frac{1}{2}$ hours the current had risen to 0.250 ampere. Red hydrate of iron, but no Prussian blue, had formed on each of the little spots where the protective covering had sealed off. The main body of the coating did not appear to have been attacked in the least. The scroll has since lain around the laboratory and been exposed to various atmospheric conditions without further change, which goes to show how energetic anodic oxidation is, particularly when assisted by a little salt.

Two days after making the test above described I took a wire nail about one-eighth inch thick and heated it to redness till it acquired a uniform coat of scale. When cold this proved to be a fairly good conductor. I made the nail an anode in a bath of 200 c. c. of 0.5 per cent KCy solution, containing KAgCy₂, to which 20 c. c. of a saturated solution of NaCl had been added. The nail was immersed about 3 inches. At 2 volts it permitted the passage of a current of 0.001 to 0.002 ampere, and was very little acted on except at the point. I allowed the current to run over night and found in the morning that it had risen to 0.100 ampere. A large quantity of a greenish-yellow slime had formed and settled out. The nail was half eaten through at the end and near the middle, but otherwise the black magnetic coating was intact. When the slimy hydrates were removed, the part eaten out below the slime was bright and white like silver. Evidently where the coating was intact it protected the iron from attack, but wherever there was a defect in the coating the iron was corroded rapidly, evidently forming a short-circuit couple between the iron and the oxide coating, which had made the corrosion more active on account of the "local action." I have experimented in this direction and have had hopes of working out a method that will give a firm coherent coating of magnetite on cylindrical iron rods, enabling the construction of a grid anode coated with magnetic oxide of iron similar to the grid anode of peroxide of lead.

Evidently in the two tests cited the "passivity" was due to an oxide film, and the explanation suggested by Faraday holds good. Films so formed are not necessarily of Fe₃O₄, as assumed by Prof. Kern, but seem to be mixtures of FeO and Fe₂O₃ in varying propor-

tions. There is more of the Fe_2O_3 on the outside and more FeO on the inside. The films are usually magnetic. The least defect in the rather brittle coating exposes the interior and corrosion ensues in a way similar to that of iron poorly electroplated with copper. The iron rusts rapidly, even under the copper coating, and scales worse than does the magnetic coating. If the magnetic coating is thick, it chips very easily, but if it is thin it seems to be porous. These defects are recognized by the Bower-Barff concern, which always dips thin light-coated grill work for interiors in melted paraffin to fill the pores in the coating. Whether a durable coating of this oxide can be obtained for anodes subject to bending and warping in handling is open to doubt.

The failure of iron anodes made "passive" in strong nitric acids, or by anodic polarization in alkaline oxidizing agents, may be due also to porosity. The film, or whatever the protecting condition is, appears to be too delicate for practical use. Grave^a claims that the pure iron is passive but the presence of hydrogen ions destroys this passivity. The "passive" state created by acid treatments is evidently too unstable to serve as the base of any industrial method in the present state of knowledge, but the importance of the subject warrants further research.

ANODES OF MAGNETITE.

Henry Blackman (U. S. patent 568231, Sept. 22, 1896) claims the use of electrically conductive anodes of iron oxide in a dense impermeable mass. He specifies the use of magnetite or ilmenite cut from a slab of the mineral, which would be a difficult task. He specifies also the agglomeration of grains of these minerals by tar or sugar or by means of suitable fluxes. This, of course, is objectionable as the binder yields and also acts as an insulating agent.

I have tried a pervious mass of loose magnetite grains held in a box with cheesecloth sides, but the mineral in this shape is neither sufficiently pervious to the solution nor of sufficient conductivity.

Heinrich Specketer (U. S. patent 931513, Aug. 7, 1909) claims the use of anodes cast in rods from molten magnetite. He fuses Fe_2O_3 , which changes on melting into Fe_3O_4 with a slight excess of FeO , the latter crystallizing in a different system from the magnetite and causing it to disintegrate. This oxide is removed by adding a small amount of finely pulverized Fe_2O_3 to the melt just before pouring into the molds. The mass solidifies on the outside first and the molten interior can be poured out, leaving a hollow tube which can be electroplated with metal on the inside, to make it a better con-

^a Grave, Ernst, Neue Untersuchungen über die Passivität von Metallen: Ztschr. Phys. Chem., Bd. 77, 1911, pp. 513-576.

ductor, or a rod of iron, copper, or nickel can be inserted in the still plastic interior. This patent has been assigned to the Chemische Fabrik Griesheim Electron, of Frankfort, Germany. The firm has undertaken its manufacture.

A part of one of these anodes, broken from a larger part, was sent me by Mr. Haigh, president of the Moore Filter Co. It was formerly used in connection with the Clancy process. The piece is of a uniform, bluish-black color, is about 10 inches long by five-eighths inch in diameter, and is cylindrical. An inch and a half near the top has been electroplated with copper to facilitate making contact. The coating is thin and has partly scaled off.

I have used this specimen as an anode in a 0.2 per cent cyanide solution without sodium chloride and sodium sulphate, with 1 per cent sodium chloride in one experiment, and with 1 per cent sodium sulphate in another, employing 4 volts, without the slightest apparent formation of either ferrous hydrate or Prussian blue, and without any change of appearance either of the anode or the solution. I did not use the anode for any great length of time, but it appears to be very durable. The outer cast surface is a deep bluish black, almost like velvet, but the fractured surface is rather bright and crystalline, like fractured magnetite. The material has the disadvantage of being brittle, but is much less so than Acheson graphite. The magnetic anode is not as good a conductor as the graphite, but is, on the whole, one of the most promising anodes that I have seen. I am informed that the material is not so permanent with an alternating current, and also that it has been abandoned as an anode for the Clancy process, being found less satisfactory than Acheson's "extruded graphite." Such graphite when soaked in paraffin is said to give better results with that process.

The permanence of the magnetite anode suggests that, in this case at least, the oxide film, as suggested by Faraday, is the true cause of the passivity. In a thin film, formed in the wet way, porosities and defects of the film may be the cause of the unreliability and frequent failures. When the film becomes ruptured, exposing only the minutest spot, an intense local action begins and destruction follows. It is possible that electrolytic lining of the hollow magnetic anode with copper in a similar way, or filling it with a rod of iron or copper while still hot, might also cause shrinkage cracks in the film and similarly result in failure.

A serious defect of the magnetite anode is that it is not a very good conductor. Landolt and Bernstein^a give for Swedish magnetite a resistance of 0.595 ohm per cubic centimeter, conductivity 1.68. I have found a much less resistance by testing the anode rod just de-

^a Landolt, H. H., Landolt-Börnstein Physikalisch-chemische Tabellen, 3d ed., 1905, p. 724.

scribed, a result which I believe to be nearer the true value. The mean of four closely agreeing tests conducted at room temperature was 0.0319 ohm per cubic centimeter (or a conductivity of 31.4). This makes the resistance nearly 20,000 times as great as that of copper, more than 3,000 times as great as that of iron, and more than 10 times as great as that of a good electric-light carbon. This is a serious drawback. Of course if the metallic core could be used, without any failure in the protecting surface, this resistance would be much cut down. Further details from the manufacturers have not come to hand.

CATHODES.

Satisfactory cathodes, as such, are not so difficult to obtain. Many suitable substances are available. But when, as in the Christy electroconcentrating process, a cathode is desired that may serve alternately as a cathode and as an anode, the problem is not so easy.

SOLUBLE CATHODES.

Mercury and amalgamated copper cathodes are specified in numerous patented processes, but serious chemical and physical objections to using these materials have been sufficiently explained. An additional objection is the cost of the large amount of these expensive metals that must be used to obtain effective deposition from the dilute solutions required in practice. Except in certain exceptional electrolytic methods where strong solutions are used and where regeneration of the cyanide and the caustic alkali is possible, it may be said that the use of quicksilver and copper is out of the question.

SHEET ALUMINUM.

The use of sheet aluminum has been proposed by Cowper-Coles,^a who claims that the cathode should fulfill the following conditions:

1. The gold should be adherent during the process of deposition.
2. The gold should be capable of being readily stripped, after removal from the electrolyzing cell.
3. The cathode should be electropositive to the gold in solution, to insure its being coated with gold on immersion.

It is affirmed that deposited gold is easily stripped from the cathodes after deposition, and claimed that the metal is recovered successfully from a solution containing 2.5 pennyweight of gold per ton and 0.01 per cent KCy. This solution is treated for 10 hours, with a flow of 15 gallons per 100 hours for every cubic foot of the deposition box, and for 3 square feet of cathode surface. Six volts

^a Cowper-Coles, Sherard. Some notes on the recovery of gold from cyanide solutions: Trans. Inst. Min. and Met., vol. 6, 1897-8, p. 219.

are mentioned as being used. However, there is great danger of the cathodes decomposing the water and becoming coated with aluminic hydrate in spite of the current, and this of course would put an end to their usefulness.

The idea of using a metal electropositive to gold to prevent re-solution of the gold in case the current fails is an ingenious one, and has been proposed by Bettal and Andreoli, both of whom use zinc for the purpose. It must be remembered that the zinc or aluminum can act as an electropositive metal and protect gold on a failure of the current only when the gold is deposited so loosely as to allow the solution access to the zinc or aluminum to form a couple. If the gold is deposited as a coherent sheet, as proposed by Cowper-Coles,^a no such protective action is possible. The anode and the gold-coated cathode then form the couple, and the gold dissolves if the current fails, in spite of the protective aluminum or zinc. Also, when mercury is in solution it amalgamates with the aluminum of the cathodes and causes the latter to heat, oxidize, and disintegrate in a most remarkable manner. In my judgment, these objections suffice to invalidate the use of aluminum for cathodes in cyanide solution.

INSOLUBLE CATHODES.

HARD CARBON AND GRAPHITE.

Hard carbon and graphite can be used in the form of sheets, both as cathodes and afterwards as anodes, in a stripping solution of pure cyanide at a low voltage without any difficulty whatever. When the gold has been concentrated on Acheson graphite sheet cathodes it may be readily stripped for the mint. It does not even need to be melted down.

There are, however, four objections to such electrodes: (1) Sheet electrodes do not offer sufficient surface to permit of rapid precipitation from dilute solutions. See the comparison of results in using sheet-iron and iron wire-cloth cathodes (p. 110). (2) Graphite and carbon in other ordinary forms are brittle, and electrodes of these materials are easily broken if much handled. (3) On account of the friable character of the material it is not possible to design a compact deposition box, as the cathode sheets must be at least one-fourth to three-eighths inch or more thick, whereas with wire cloth five times the precipitating surface may be provided in the same space. (4) The electrodes are costly. However, notwithstanding all these drawbacks it must be said that such electrodes furnish a physically workable solution of the difficulty.

^a Cowper-Coles. Sherard. Some notes on the recovery of gold from cyanide solutions: Trans. Inst. Min. and Met., vol. 6, 1897-8, p. 219.

SHEET IRON.

Gold comes down very well on a surface of sheet iron; but, as already pointed out, the defect of plane sheets is the lack of sufficient precipitating surface. I have not found it necessary to scale the sheet iron by pickling; the electrolytic current soon precipitates enough gold and silver to cover the magnetic oxide scale, and in time the action even will cure rusted surfaces. It is, of course, an added expense to subject electrodes to pickling, and the cost of this would be considerable. The method of pickling suggested by Julian and Smart^a is as follows:

We have also used iron with success (as cathodes), and we find that in order to get the best results all the oxides should be removed from its surface. This we have done by immersing the plates in the following mixture: 100 parts of water, 10 sulphuric in which 1.5 of zinc is dissolved, and then adding 10 of nitric acid. If then washed in an abundance of water and kept in an alkaline solution they remain nearly as bright as silver. In this state they receive a perfectly uniform deposit. Lead can not be used to remove the deposit, as this injures the iron surface for reuse, but if placed in narrow iron boxes containing 2 to 5 per cent KC_Y solution and connected with Daniell cells in parallel to form the anode, while the box is the cathode, the gold and silver rapidly dissolve off without reprecipitating, leaving the plate perfectly bright and clean and ready to go back into the precipitating box.

The solution is then evaporated to dryness and melted to get the gold.

This method would be more expensive than ordinary pickling, but I can testify that it gives good results. The plates remain bright in alkaline solutions almost indefinitely. Even when used as anodes, with a voltage below 1, such plates stand up fairly well, but at higher voltages they oxidize as badly as ordinary iron. The metal can hardly be said to be "passive" when it acts as a cathode. It is possible that a film of zinc forms on its surface, although this seems improbable in the presence of nitric and sulphuric acids, or the film may be nitride of iron. At any rate the surface seems to be more permanent than "pickled" iron surfaces usually are.

As I have already pointed out, the intermittent nature of the experiments introduces a difficulty that would not occur to the same extent in continuous operation. At the end of a run the iron wire-cloth cathodes with gold or silver deposited on them had to be removed from the cyanide solution. It was not feasible to dry them by artificial heat, because the uneven expansion of the metals might cause scaling. If allowed to dry in the air at room temperatures the dampness of the wires soon caused local action, gold and silver were attacked slightly and dissolved in the cyanide solution with which the wires were wet, and after the cyanide was exhausted the

^a Julian, H. F., and Smart, Edgar. Cyaniding gold and silver ores, 1904, p. 140.

ron began to rust by local action under the coating. This trouble appeared when the cathodes were again returned to the deposition ox, and, as has been seen, during the first hour or more the old and silver dissolved in spite of the current. Not until the rust ad been reduced was the gold again precipitated. In continuous work the cathodes would remain in the deposition box till they were o go into the stripping box, and when stripped they would go back unto the deposition box. The difficulty would not then appear to he same extent. However, it was highly desirable to cure the evil itogether.

Many devices were resorted to. Among others the cathodes were mmerged in gasoline or refined petroleum as soon as removed from he deposition box. As these liquids contained no oxygen, it was oped to preserve the cathodes from rusting. They have such an effect, except at some points where occluded oxygenated water remained and acted. But a worse evil arose. The gasoline, like all etroleum products commercially applicable, contained so much issolved heavy hydrocarbon that when the cathodes were removed or use an insulating residue was left on the entire surface, rendering hem almost nonconductors. It is possible that the cathodes might ave been preserved if they had been dried in vacuum and kept in vacuum. But this did not appear to be practicable.

Heating the iron-wire gauze to redness in an atmosphere of ammonia gas was tried. Hydrogen was set free and nitride of iron f a silver-gray color formed, and the cathodes no longer rusted in ny ordinary atmosphere. A piece of such gauze so treated has een exposed 10 years to the atmosphere of the laboratory without erceptible change. But the treatment had made the wire brittle s a pipestem, and when used as an anode under a strong current it ailed as before. Possibly such a treatment might be used if it were ot pushed too far, but the extreme brittleness resulting led me to rop the method.

PLATINUM.

Cathodes of platinum-wire gauze of 16 meshes to the linear inch, f 0.5-mm. wire, united like those of iron-wire cloth into "bunches f five," would be satisfactory as regards both rapid precipitation nd perfect stripping. Some method of rapid drying would still e necessary to avoid resolution of the deposited metal in interruttent use, but the undercutting by rusting would have been voided. However, calculation soon showed that the cost of such athodes was prohibitory, and I was forced to compromise. I or-ered some wire-cloth cathodes of 16 mesh (linear) to be made by Iereaus in Germany. The metal used was platinum with 10 per ent iridium, but the wires were only 0.1 mm. in diameter and the

conducting wires welded to the edge of the cloth were 0.5 mm. thick. The cathodes were made 11 by 11 cm. in size, with an ebonite frame at the edges to give the required stiffness. The section exposed to the solution was 10 by 10 cm. The 88 electrodes cost, at the price then prevailing, in 1902, nearly \$250. Seventy-two of these anodes and cathodes, with insulators, could be compacted into an 8-inch length of box with an effective section 4 by 4 inches, or into 128 cubic inches, or 0.074 cubic foot. That would have made a total cost for electrodes of \$2,900 a cubic foot. At the rate of even 1,000 cubic feet of solution treated a day in such a box, or 31 tons a day, or 11,315 tons a year, the interest on the cost of the platinum would be \$145 a year, or \$0.0128 per ton of solution precipitated. At the present prices of platinum this item would be far greater. The cost alone would be excessive; but the platinum cathodes at the start had only one-fifth the precipitating surface of the iron ones, and the precipitation was at only about half the rate at best. As they became coated with gold and silver, however, the area would increase, and the precipitating rate would increase correspondingly until the gauze would be choked with deposited metal.

The use of iron-wire gauze electroplated with platinum, or composite wires with an iron core and a platinum face drawn down through draw plates, might be feasible. But I had doubt as to whether a layer of platinum as thin as it would be economical to employ would be impervious to the OH ions. If the platinum were not impervious, the electrode would soon be destroyed. The ends of the composite drawn wires would also be a weak point for attack.

The most favorable ratio between wire diameter and distance between wires to give maximum depositing area with minimum resistance to flow of solution is when the diameter of the wire is one-third the distance between the wires, center to center, as can easily be shown mathematically. If this ratio is maintained, the total wire surface (warp and woof together) is a little more than that of both sides of a solid sheet of metal. Diameters of wire between 0.5 and 1 mm. give the best results.

IRON-WIRE CLOTH.

The many advantages of iron-wire cloth cathodes, such as the large precipitating area, the dense current that they will endure, their great permeability, and the compactness of design which they lead to, have made me very reluctant to abandon them. As before explained, the oxidation by "local action" between experiments followed by subsequent rusting and resolution would not occur in continuous use. Very little oxidation occurs in the stripping box if the stripping current is kept below 1 volt. In order to prevent leaving the electrodes too

long in the stripping box, which would be wasteful of current and would be attended with other bad effects as is claimed by Uslar,^a they could be suspended in the box by using a device like Roseleur's plating balance described by McMillan.^b This could be made to break the stripping circuit automatically and sound an alarm if thought necessary. Anodes of carbon or of melted magnetite could be used when desired to recover the dissolved gold in sheets at a slightly higher voltage from the clean-up solution. As the stripped cathode that has served as the anode of the clean-up box would be wet with a rich solution, and would have suffered an incipient oxidation, it would be inserted first as cathode for a few minutes in the so-called "hospital cell." This cell would contain 1 or 2 per cent caustic potash or soda, and with 4 or 5 volts a strong current giving a violent evolution of hydrogen would soon bring back any oxidized spots into such a state that they would be at once effective when again inserted in the deposition box.

When iron-wire cloth cathodes have become badly rusted they are easily brought into normal condition by heating in a closed iron box to about 400° C. (below red heat) in an atmosphere of hydrogen, carbon monoxide, or vapors of gasoline. Care must, of course, be taken to displace the air from such receptacle by the reducing vapor before applying the heat. The excess vapor used for the reduction would be burned, outside the box, in a suitable burner to furnish the heat necessary for the reaction. The cathodes, when badly rusted, may be brought back to duty by immersing them in powdered charcoal and heating them to a temperature below redness. Care should be taken not to overheat and melt them.

PERVIOUS CATHODES OF BROKEN COKE, CARBON, OR GRAPHITE.

In order to escape the difficulties with the iron-wire cloth cathodes I have tried also pervious cathodes composed of $\frac{1}{8}$ -inch fragments of hard coke, as well as retort carbon and graphite. Cathodes of these materials were formed by placing the material in boxes having cheesecloth sides, so that the solution could flow through the mass. On April 5, 1904, I was granted United States patent No. 756328 for a process of recovery of gold and silver from cyanide solutions along these lines. Figures 30 and 31 taken from the patent specifications will serve to illustrate the devices used.

The general process is shown in diagram 1, figure 30. *B* is the storage tank for the solution; *A*, the deposition box or electrochemical cell. The figures shows the anodes *d* (marked +) and the

^a Von Uslar, Manuel, and Erlwein, Georg. Cyanid-Prozesse zur Goldgewinnung: Monograph, angew. Elektrochemie, Halle, Germany, 1903, 100 pp.

^b McMillan, W. G., Treatise on electro-metallurgy, 3d ed., 1910, p. 101.

cathodes *c*, marked with a minus (-) sign. These are connected in parallel with a shunt-wound or separately excited dynamo *D*, provided with a suitable ammeter *F* and a voltmeter *C*. The solution

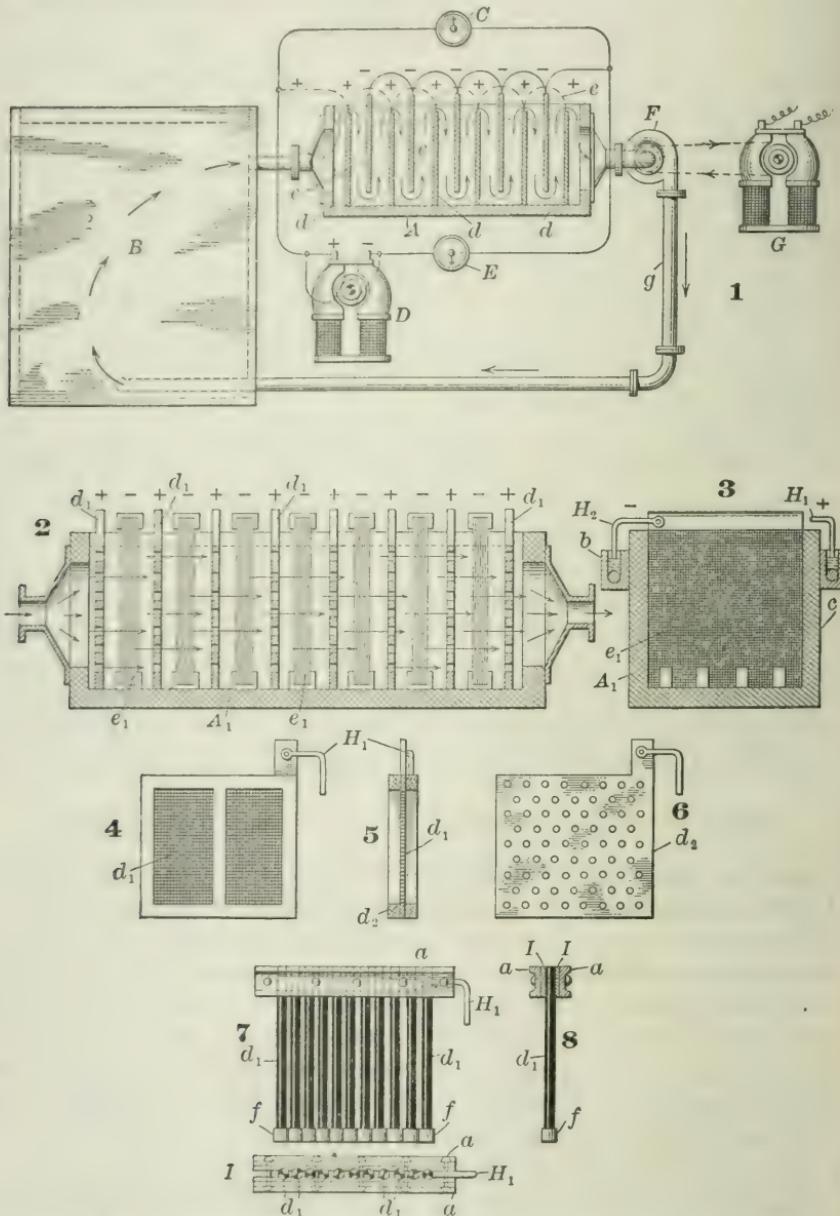


FIGURE 30.—Apparatus for recovery of gold and silver from cyanide solutions.

flows through the deposition box *A* from the tank *B* through a suitable centrifugal pump *F*, driven by a motor *G*, and back again through pipe *g* to the tank, and so on, rapidly, continuously, and

repeatedly and in such a manner that the solution is brought into intimate contact with anodes and cathodes in rapid alternation until

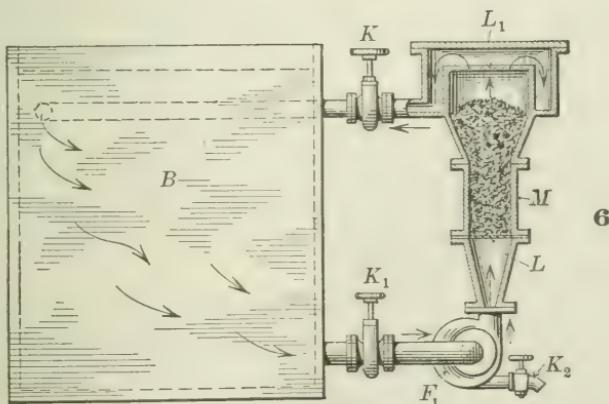
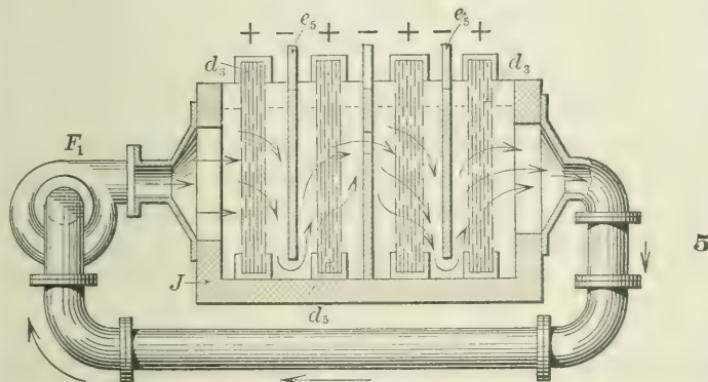
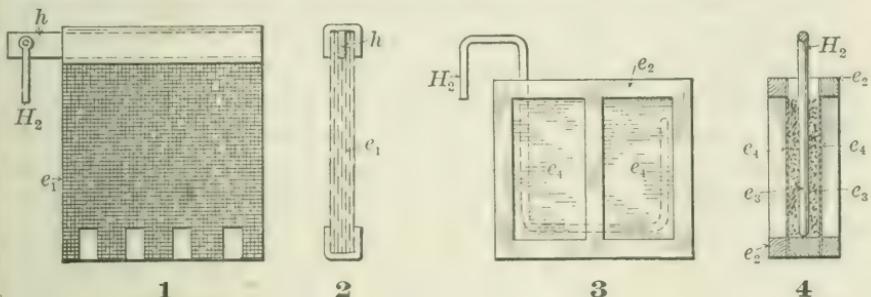


FIGURE 31.—Details of electrodes and of deposition box. Lettering similar to fig. 30.

the gold and silver content has been sufficiently reduced, when the solution is discharged and a new lot treated.

Diagram 1 of figure 30 shows also the common form of deposition-box A , with removable cathodes e . The solution flows in a zigzag course through the box, as is indicated by the arrows; but the form of deposition box or electrochemical cell that I prefer is one with pervious electrodes, as shown in diagrams 2 and 3, figure 30. In these diagrams the box is designated by A_1 , the anodes, d_1 , are marked with the plus sign (+). The anodes are made of any electroconducting substance not too much acted on by the solution, such as iron, lead, peroxide of lead, platinum, or, for pressures not greatly exceeding 1.5 volts, dense carbon or graphite. These anodes may be constructed of wires, rods, gauze, or perforated sheets, in any form or manner to be pervious to the solution. The wire-gauze d is best mounted to prevent contact with the cathodes, in a parafined wooden frame d_2 as in diagrams 4 and 5, figure 30, connected electrically with an amalgamated copper wire H_1 . The perforated sheet-metal anodes d_2 are constructed as in diagram 6, figure 30. The graphite or carbon anodes may be similarly constructed of perforated blocks; but I prefer to construct them of the densest graphite or electrode-carbon rods d_1 , mounted, as in diagrams 7, 8, and 9, figure 30, in which a represent parafined wooden frames, inclosing electroconducting strips I , which are connected with the amalgamated copper wire H_1 . The electroconducting strips make electric contact with the carbon rods placed about one-eighth inch apart. At f short strips of rubber hose are shown which prevent contact with the cathodes.

METHOD OF PREPARING AND USING PERVERIOUS ELECTRODES.

When wire-cloth cathodes are used the wire cloth is cut to a size to fit the box, and the sheets e_1 are clamped together, as in diagrams 1 and 2, figure 31, in bunches of five or ten sheets, electrically connected with a sheet-iron strip h , to which is riveted an amalgamated copper wire H_2 . Before the sheets of wire gauze are clamped together they should be preferably heated to dull redness for about one minute to burn the oil usually left on the surface by the manufacturer and to coat them with a thin coating of magnetic oxide of iron. They should not be exposed to the heat too long or a thick scale forms that easily cracks off.

Instead of iron-wire gauze any other pervious conducting substance may be used as a cathode, such as metallic filaments or cloth saturated with precipitated silver, gold, or other metal, thus exposing a large surface. A metal surface of this kind may be prepared by inserting a sheet of metallic wire cloth (of iron, for instance) as a basis for a cathode, into a suitable electrochemical cell provided with pervious anodes. Through this cell is circulated a strong solu-

tion of gold, silver, copper, lead, or other electronegative metal, during the passage of a dense electric current, to precipitate such metal on the surface of the wire cloth in a pervious or spongy layer. This forms an electrolytic filter of enormous cathode area in a small compass. The anodes and cathodes thus formed may be arranged as shown in diagram 2, figure 30, or they may be arranged horizontally one above the other and the dilute cyanide solutions from which the gold and silver are to be removed may be forced to circulate rapidly through such pervious anodes and cathodes.

Also, for the purpose described, granulated metal, pulverized coke, or electrocarbon dust e_3 , properly sized, may be placed in a wooden framework e_2 , covered with cheesecloth e_4 , and electrically connected by an iron wire ending in an amalgamated copper wire H_2 , as shown in elevation in diagram 3, figure 31, and in cross section in diagram 4, figure 31. The electrodes are separated one-half to one-fourth inch to prevent short-circuiting. In diagrams 2 and 3, figure 30, is shown the arrangement of such a deposition box with pervious anodes and removable pervious cathodes. Electric connections in parallel are made with the anodes and cathodes, as shown in the sectional view 3, figure 30, by the box b , connected with the negative pole, and by the box c , connected with the positive pole of the dynamo. The wooden boxes b and c contain omnibus bars of amalgamated copper and connecting holes filled with mercury, into which dip the wires H_1 from the anodes and the wires H_2 from the cathodes.

The box A_1 , shown in diagrams 2 and 3, figure 30, is placed in the position shown for box A in diagram 1, figure 30, being substituted for that box, and the solution is forced to circulate repeatedly from tank B through the box A_1 and through the pervious anodes and cathodes, and back again, so as to be brought into intimate contact with anodes and cathodes in rapid alternation until its gold and silver content is sufficiently reduced. When the voltage is kept constant at any point (at two volts, for instance) the completion of the treatment is indicated by the number of amperes of the electric current. The number is high at first, but suddenly drops and becomes constant when the gold and silver content of the solution is exhausted. Since the fall of electric current could be caused by an accidental increase of resistance, it is necessary always to assay the solution before discharging the lot under treatment.

I prefer to concentrate the gold and silver thus deposited on removable cathodes in the manner shown in my former patent, No. 643096, February 6, 1900. However, I have been able to increase the precipitating capacity of the deposition box by the new method described here to far exceed the capacity of the clean-up box there shown. I have also been able to apply the same principle of rapid

circulation to that box, and thus to increase its capacity. Diagram 5, figure 31, shows how this is effected. A centrifugal or other pump F_1 forces the cyanide solution, which should be as free as possible from chlorides and sulphates, to circulate rapidly through the clean-up box J , preferably, though not necessarily, at such a rate as to prevent the evolution of gas at the cathodes. These consist, preferably, of sheets of iron e_5 , marked with a minus (-) sign in the figure and arranged, as shown, to force the solution to pass alternately up and down through the box and at the same time through the pervious secondary anodes d_5 , marked with a plus (+) sign. These secondary anodes are the gold and silver laden primary cathodes e_1 , from the deposition box, shown in diagrams 2 and 3, figure 30. Although pervious cathodes e_1 to collect the silver and gold in the deposition box are preferable, impervious cathodes, e , shown in diagram 1, figure 30, can be used. The gold and silver content is then concentrated on the secondary cathodes in a similar manner. The secondary cathodes e_5 , of sheet iron or other metal, marked minus (-) are, before being inserted in the clean-up box, coated with a very thin layer of electroplater's graphite and vaseline. With an electromotive force of about one-half volt, the gold and silver are rapidly removed from the removable secondary anodes d_5 (primary cathodes e_1 in the deposition box) and deposited on the secondary cathodes e_5 , as solid sheets. These sheets may be pulled off at convenient intervals and are ready for the mint without further treatment. I have thus produced solid sheets of bullion one-eighth of an inch thick and 996 fine. If an extremely dense electric current is used in the clean-up box, the gold and silver will be deposited on the secondary cathodes in the form of a loose powder, which is easily removed with a stiff brush and can be melted down into bars. The rapid circulation of the solution permits the concentration of the metal with a dense current, and greater rapidity is insured in a small box.

Also, it is evident that, instead of having two separate boxes—a deposition box and a clean-up box—the same result may be obtained with a deposition box that serves both purposes in alternation. This is particularly the case when pervious cathodes of broken carbon or graphite are used, for these are bulky and inconvenient to remove to a clean-up box. Instead of doing this, when the cathodes become sufficiently charged with gold and silver in the deposition box after the circulation of a large volume of cyanide and ore solution, the circulation from the storage tank is cut off. Then the same or a fresh cyanide solution is made to circulate rapidly and repeatedly through the box (see diagram 2, fig. 30) by means of a pump, as in diagram 5, figure 31, except that now the primary cathodes of diagram 2, figure 30, marked minus (-), are connected with the plus

(+) pole of the dynamo, to become secondary anodes, while the original anodes (diagram 2, fig. 30), marked plus (+), are replaced by secondary cathodes of sheet iron which have been previously coated with a mixture of graphite and vaseline. The secondary cathodes on being connected with the negative (-) pole of the dynamo become coated with the gold in a concentrated form, which had been previously distributed on a very large primary cathode area. The secondary cathodes may be of the form of those marked minus (-) in diagram 5, figure 31, or they may be as shown in diagram 6, figure 30, or they may be of separate strips of iron or other conducting material, arranged like the slats of a window blind, so as to be pervious to the solution. It is preferable to circulate the solution at such speed that evolution of hydrogen gas is practically avoided at the cathode; if, owing to the density of the electric current used, this is not possible the velocity should not be less than 1 foot per minute. When the gold content of the original cathodes, now secondary anodes, has been recovered, the secondary cathodes, now laden with concentrated gold, are removed, the original anodes are replaced, the electric connections changed to the original condition, and the stock solution turned again through the tank, which now serves as a deposition box, as shown in diagrams 1 and 2, figure 30.

The same principle of rapid circulation and repeated treatment in rapid alternation of a large volume of solution in a small deposition box containing pervious electrodes may also be applied to the electrochemical recovery of gold and silver from cyanide solutions without the use of a dynamo or external source of electricity, the electric energy being furnished by such an electropositive metal, as zinc, in the form of fine granules, shavings, or dust. This system is shown in diagram 6, figure 31. The figure shows at *B*, the large storage tank containing the solution to be treated, a centrifugal or other pump *F*₁, and a vessel *M*, containing zinc in the form of shavings or other form, exposing a large surface. The zinc rests on a filter *L*. A filter *L*₁ may be used at the top of the box to avoid the loss of fine particles, if desired. *K*, *K*₁, and *K*₂ represent valves to control the flow. The solution is forced to circulate from the tank *B* through the zinc and back again repeatedly (preferably, though not necessarily) at such a rate as to substantially prevent the evolution of hydrogen. The gold and silver are rapidly precipitated by the electrolytic action set up between the solution and the zinc. The zinc particles act as anodes and the gold and silver particles, which are at once deposited in a porous or pervious state upon the zinc, act as cathodes. The zinc anodes covered with this pervious coating of gold and silver form a combination of pervious anodes and cathodes, and when the solution is forced to circulate rapidly and repeatedly through them it is brought into intimate contact with anodes and

cathodes in rapid alternation. Although the electromotive force of the combination is small, the current is short-circuited, and the resistance therefore is smaller than in any other form of cell, and hence the gold and silver are rapidly precipitated. In this type of process it is important that the gold and silver be precipitated on the zinc in a loosely adherent porous film in order that the zinc and the precipitated metal form a set of electrodes pervious to the solution. In some instances the precious metal forms a solid impervious film on the surface of the zinc. When this happens, precipitation ceases. In such an event the zinc, before use, should be coated by dipping it into a dilute solution of nitrate of silver or acetate of lead, forming a pervious film of silver or lead. When the zinc is sufficiently fine the precaution is unnecessary.

By the ordinary zinc process, owing to local action, 5 to 20 ounces of zinc are required to precipitate 1 ounce of silver or gold, but with the Christy process practically complete precipitation of 1 ounce of silver with 0.57 ounce zinc has been effected, and results nearly as good with gold. In practice the use of about 2 ounces of zinc to 1 of gold and silver is preferable, but even then the use of the process will save zinc and reduce the cost of refining the precipitate.

By the application of the same principle the precipitate can be refined without the use of acid by circulating rapidly and repeatedly a solution of cyanide, nitrate, or sulphate of silver, of cyanide or chloride of gold, or soluble salt of copper, through the precipitate, so that such solution may come into contact, in rapid alternation, with the residual particles of zinc, acting as pervious anodes, and of deposited gold and silver, acting as pervious cathodes, until the residual zinc is dissolved. After refining the precipitate in this manner the silver or gold, left in the refining solution, is recovered by the use of fresh zinc, as before.

Most of my work, though not all, was done with pure solutions, and desiring to see how the process would work with stock solutions from the treatment of ores, I obtained in 1905, through the kindness of Mr. Charles Rhodes, manager of the Waihi mine, New Zealand, and of Mr. W. W. Mein, general manager of Robinson mine, Johannesburg, an opportunity to have tests made at these places.

I much appreciate the trouble the experimenters took with these tests, but none of the experiments were carried out exactly as I directed. In some tests the lack of facilities at hand made this impossible; in others the ideas of the experimenter led to changes in details without realization of the detrimental effect. Most serious of all was the failure to record all the necessary variables. Thus the causes of success or failure in many of the experiments can not be determined. Circulation by means of the pump, which should have been easily controlled, was found troublesome and results in

some tests seem to indicate that the boxes did not get the proper treatment. I present here the results obtained by other men in tests conducted at my request as described.

EXPERIMENTS AT WAIHI MINE, NEW ZEALAND.

The experiments at Waihi mine, New Zealand, were conducted by Herbert W. Hopkins, metallurgist, Victoria mill, Waikino, in 1905.

The solution employed for these tests was that which had been used in treating a clean gold and silver bearing quartz ore containing 1 per cent pyrite. The solution was heavily charged with lime to settle the slimes. The box used was 3 feet 4 inches by 1 foot by 10 inches. The electrodes were immersed to present an area 11 by 9 inches, which later was increased to 11 by 10 inches.

EXPERIMENTS WITH FLAT OR PLANE ELECTRODES.

SERIES A TESTS.

Both the 29 anodes and the 28 cathodes were of lead. No trouble is mentioned with respect to the anodes, and it is presumed that they were peroxidized. The cathode area exposed was 38.5 (later 42.8) square feet for both sides and all electrodes were spaced one-third inch apart. Allowing one-eighth inch for thickness of lead, we have 1.66 cubic feet as the volume of box actually occupied by electrodes. The capacity which I claimed such a box should possess was 8.30 cubic feet per 24 hours.

Twelve experiments were made with a single flow through the box at a rate varying from 0.75 to 0.87 long ton, or 26.7 to 31 cubic feet per 24 hours, which is three to four times the capacity claimed for such a box. With 2.5 to 3 volts and 3.5 to 3.8 amperes and an average current density of about 0.1 ampere per square foot, the average of 12 experiments was a recovery of 32.3 per cent gold and 31.2 per cent silver, with a reduction in cyanide content of the solution from 0.142 to 0.138 per cent. If the volume treated had been reduced to 8.3 cubic feet per 24 hours, the results would undoubtedly have been much the same as I have obtained.

SERIES B TESTS.

Three experiments were conducted with 6.1 cubic feet of solution passed four times through the cell in 3 hours, which would be at the rate of 48.8 cubic feet per 24 hours. With 2.5 to 3.5 volts and 3.5 to 10 amperes no gold was obtained. The current density here was 0.26 ampere per square foot, or nearly the same density as that used by Mr. Butters to deposit metal as a slime, and the rate of passage of the solution was about 5.88 times that which I have desired. The

velocity of flow of solution through the narrow slit between the plates, $\frac{1}{2}$ by 11 inches, would have to be more than 5 feet per minute to give this flow, hence it was to be expected that the loose slimy deposit would be stripped from the flat plates by the excessive flow.

SERIES C TESTS.

In this test the rate of flow was 0.92 long ton or 32.15 cubic feet per 24 hours, nearly four times the desirable capacity of the box. At 4 volts and 10 amperes and with a density of current amounting to 0.26 ampere per square foot the recovery of gold was 61.7 per cent and of silver 59.3 per cent, with no loss in cyanide. Considering that this is nearly four times the desirable capacity of the box, the results are not bad. The current density was sufficient to deposit slime on the flat electrodes, but the circulation was not sufficiently violent to wash it all off. Another experiment, at the rate of 0.9 long ton per 24 hours, gave 60.7 per cent recovery of gold and 59.8 per cent of silver.

In all the above experiments with flat electrodes the volume of solution was three to seven times greater than the capacity which I should have desired. As the duration of the tests is not mentioned the ampere-hour efficiency can not be calculated.

EXPERIMENTS WITH PERVERSIVE WIRE-CLOTH CATHODES.

The solutions employed in the tests with perversive cathodes contained 7 to 25 pennyweights of gold per long ton, 1 to 3 ounces of silver, and 0.14 to 0.22 per cent potassium cyanide. The 28 cathodes and 29 anodes were spaced one-half inch. Each cathode was a single piece of 16-mesh iron-wire cloth, the total area being about 34 square feet. The anodes were of sheet lead resting on the bottom of the box and perforated by 80 one-half inch holes. These should have been five or ten times as numerous.

For the test a measured quantity of solution was placed in a barrel at the head of the deposition box, also filled with the solution. The current was allowed to run from the barrel through the box to a second barrel which received the tailing. At the end of the test the content of this tailing barrel was transferred to the head barrel. Later, after experiment 25, two head and two tailing barrels were used, to make sure that every part of the solution received its proper treatment.

Three interesting experiments, which will be here designated A, B, and C, were made to determine the effect of a stoppage of the dynamo. The conditions of test and results were as follows:

A. Solution standing in cell; dynamo stopped; brushes down; circuit not broken. Sample taken when dynamo stopped: Gold content, 5 pennyweight 5

rains; silver, 14 pennyweight 21 grains. Sample taken after standing 16 hours: Gold content, 6 pennyweight; silver, 16 pennyweight 5 grains.

B. Solution standing in cell; dynamo stopped; circuit broken. Sample taken when dynamo stopped: Gold, 15 pennyweight 12 grains; silver, 2 ounces 2 pennyweight 9 grains. Sample taken after standing 20 hours: Gold, 16 pennyweight 11 grains; silver, 2 ounces 5 pennyweight 20 grains.

C. Solution standing in cell; dynamo stopped; circuit broken. Sample when dynamo stopped: Gold, 5 pennyweight 23 grains; silver, 9 pennyweight 11 grains. After standing 1½ hours: Gold, 5 pennyweight 21 grains; silver, 10 pennyweight 18 grains.

The longest stoppage that occurred during which the circuit was broken was one hour.

Allowing one-eighth inch for the thickness of the electrodes, which were one-half inch apart, the electrodes occupied 2,200 cubic inches, or 1.25 cubic feet. Thus the box was much less compact than those which I have used with wire-cloth electrodes, in which the current gap was never more than one-fourth and often less than one-eighth inch, and in which I never found indications of short circuits.

DISCUSSION OF RESULTS.

It will be observed that the best results of the experiments between Nos. 21 and 28 were obtained with rich solutions, test 24 giving the best results of all. The experiments ran too short a time, probably because the handling of the barrels was too onerous. The centrifugal pump would have removed that difficulty. If the cathodes were intermittently used, rusting and subsequent stripping must have taken place and lowered the results during the short time of the test.

In experiment 36 the wire cloth was 8-mesh. Only three sheets were placed between each cathode; hence adequate depositing surface was not provided. Though most of the solution passed beneath the cathodes, some must have passed through. The cathodes had evidently rusted with some gold and silver upon them from a previous experiment. This corresponds with my own experience. Then when the cathodes were used in experiment 36 the gold and silver immediately redissolved where the cathode had rusted, and until the rust was removed the current was wasted in reducing the iron oxide. The silver, being easier to reduce, came down first. Experiments 37 and 38 seem to show that the cathodes were in better condition; and though the current density is still high, the ampere-hour efficiency is fair. If these experiments had been conducted exactly as directed, the results obtained would have been better. Foul mill solutions are harder to treat than clean solutions. I have successfully treated many such solutions, as well as similar solutions saturated with lime. The solutions at the Waihi mine contained, among other substances, selenium, probably as selenate of sodium,

which is usually recovered with the gold and silver in the zinc clean-up. The real difficulty in the last experiments was doubtless the rusting of cathodes, through intermittent use. One of the cathode plates sent me, though carefully packed, was covered with rust.

EXPERIMENTS AT TRANSVAAL GOLD MINING ESTATES.

Some experiments were made with iron-wire cloth cathodes at Transvaal Gold Mining Estates, Pilgrim's Rest, South Africa, by A. Serymgeour in August, 1905. The description given here is condensed from a report presented by him to W. W. Mein. The precipitation box used was of 1 cubic foot capacity, the cross section not being stated. The anodes were one-sixteenth inch iron plates with one-fourth inch holes. The cathodes were of wire gauze, the mesh, area, and construction not being stated. The first experiments were made with working solutions containing an average of 4 penny-weights gold per ton, copper as a double cyanide, and 0.016 per cent and 0.0087 per cent cyanogen and protective alkali. A long series of experiments gave an average precipitation of about 25 per cent of the gold after a half hour's contact.

The average precipitation of our ordinary Siemens and Halske box is 75 per cent for four hours' contact (eight times as long), so that the Christy method panned out appreciably better, but against that there is the fact of clean anodes and higher amperage. As there was, however, a considerable discrepancy between these results and Prof. Christy's, a clean solution of sodium aurocyanide was made up and a series of experiments done therewith.

The precipitation was most exceptional—75 to 80 per cent on half an hour's contact. With clean solutions of aurocyanide the iron plates were scarcely attacked, but with working solutions the plates became extremely foul with iron and copper cyanides and had to be cleaned up every week, the resulting "blue" containing 7.9 ounces to the ton, which is extremely high for so short a period.

With working solutions the free cyanide was consumed to the extent of about 25 per cent.

The very high rates of flow (1 foot a minute) mentioned in Prof. Christy's paper gave practically no precipitation. One foot in four minutes seemed most effective in our experimental box.

The wire-gauze cathode gave a very nice and clean deposit.

In this brief report some details are missing. The section of the cathodes, the skin area of their surface, the current density, the current, and the voltage, are not stated; therefore it is not possible to explain the low result obtained at the rate of flow of 1 foot per minute. With the foul solutions treated, iron anodes should not have been used, but, instead, perforated peroxidized lead anodes. The presence of copper, moreover, introduces difficulty in the precipitation of the gold by any process, as will be considered later.

EXPERIMENTS WITH PEROXIDIZED ANODES.

These experiments, like those previously described, were conducted in the latter part of the year 1905 by A. Scrymgeour on copper and gold bearing cyanide solutions. The lead plates were peroxidized in permanganate of potassium solutions and were one-fourth inch thick, with five-eighth inch holes. The holes were too large and were probably too few in number. The results were better than with iron anodes.

"The cathode gave, upon the whole, a good deposit, but a slight furring of the copper was noticed at the higher amperages." The solutions treated contained 0.046 to 0.065 per cent copper, 0.004 to 0.006 per cent alkali, and 0.0064 to 0.013 per cent cyanide. The rate of flow varied from one-eighth to one-third of a foot per minute, and the current was 0.014 to 0.033 ampere per square foot of cathode surface. The original content of gold was 1.05 to 2.2 pennyweights, which after one hour became reduced to 1.25 and 0.3 pennyweight, with 16 to 71 per cent recovery. In this and in other experiments there were evidences of cathodes having rusted from intermittent use.

In one test a clean solution of sodium aurocyanide was treated, the rate of flow being one-eighth foot per minute and the current 0.014 ampere per square foot. The original content was 2.2 pennyweights, becoming reduced after one-half hour to 0.40 pennyweight, and after one hour to 0.10 pennyweight, showing an extraction of 95 per cent. In only one or two tests was there any evolution of gas. The current density used by Siemens and Halske is given as only 0.006 ampere per square foot, and Scrymgeour, judging by that, evidently thought it best not to push the current density too far. The density, however, was not sufficient to insure a good precipitation. The best results were obtained with the higher current densities.

EXPERIMENTS AT ROODEPORT CENTRAL DEEP, 1905.**FIRST GROUP TESTS.**

In 1905 some experiments were made at Roodeport Central Deep mines, in South Africa, by Gabriel Andreoli. In these experiments, after some preliminary work with low current densities, similar to those usual in the Siemens & Halske process, the box was operated at such a density as "to just allow a slight evolution of gas to be visible at the electrodes." To quote further from Andreoli's report:

The results of this experiment being in my opinion very encouraging, it will perhaps be interesting if I give full details:

Space of box occupied by anodes and cathodes, slightly under 1.5 cubic feet, say 90 pounds.

Flow of solution through box maintained during the experiment at 4 pounds per minute (0.0632 cubic feet per minute or a velocity through box=0.77 inches per minute) - duty 64 times capacity of box.

Twelve anodes 1 foot square of $\frac{1}{8}$ -inch sheet iron perforated with $\frac{1}{4}$ -inch holes; 24 cathodes in pairs, each cathode consisting of five sheets of mill screening clamped and connected together, $\frac{1}{2}$ -inch space between anodes and cathodes. Current at start 10 amperes, slight evolution of gas apparent, current subsequently reduced in stages to 7 amperes, maintaining evolution of gas at electrodes.

KCy and alkalinity tested right through the experiment, and practically no alteration, KCy 0.068 per cent, alkalinity expressed as $\text{NaHIO}=0.0218$ per cent.

Value of solutions:

Before first circulation, 8.04 pennyweights per ton.

After first circulation (drip sample at foot of box) 1 pennyweight per ton.

Recovery, 87.5 per cent. Duty, 64:1.

Before second circulation 3.66 pennyweights per ton.

After second circulation 0.6 pennyweight per ton.

Recovery, 81.4 per cent. Duty, 64:1.

Total recovery, 91.5 per cent. Duty, 32:1.

If it had not been for the accident of mixing the 1-pennyweight solution with some of the original solution I feel certain that the total recovery would have shown a more striking figure.

As it is I consider this very successful as compared with the Siemens & Halske process which in this plant gives an average recovery from solutions of only 70 per cent and the duty compared to capacity being 2.5:1.

The experiment, however, seems to contradict Prof. Christy's claims that the process is economical from an electrically efficient point of view. I may later on succeed in obtaining good precipitation with a lower current density, which was in this experiment extremely high, namely, 0.3 ampere per square foot of anode surface. Normal Siemens & Halske practice here is 0.04 ampere per square foot of anode surface.

If it is found that such a high current density is necessary for successful precipitation then insoluble anodes will be indispensable; but to any one accustomed to the so-called Prussian blue produced on a Siemens & Halske plant, its treatment is not a formidable matter.

In the three experiments the gold precipitated on the cathodes was in the form of a bright deposit with perhaps the exception of the last experiment, where the gold on the lower part of the box was inclined to be slimy, but this was to be anticipated, considering the high current density used.

In regard to the statement that the electrical efficiency is below that which I have found it to be in my own experiments, I may say that my own experiments are perhaps a sufficient answer and that no data were given to justify criticism. The voltage, the duration of the test, the quantity of solution treated, and the average number of amperes are not given by which the results might have been calculated. Moreover, it was afterwards found that the tanks used were old chlorination tanks already saturated with gold, which introduced a handicap that no process would overcome.

SECOND GROUP TESTS.

The following description of further experiments at Roodeport, in 1905, is from the report that Andreoli rendered to Mr. W. W. Mein:

From the results I have obtained so far it is noticeable that I have only had satisfactory results on the occasions when a heavy current density has been used, and the production of by-products due to the use of iron anodes has been considerable; and on the lines which I have been working the use of insoluble anodes appears imperative. I have communicated with you, and a set of peroxide of lead anodes is being made.

As you will notice from the results obtained in experiment 6, the duty of the box is considerably higher than anything the Siemens & Halske process has approached, besides being much more effective, but the competition to be met from the Siemens & Halske process is negligible; it is the ordinary zinc precipitation which has to be met. Here again experiment 6 gave an equal precipitation result at a higher proportion of daily flow to the capacity of the box than even the zinc process and with the expenditure of more electrical power. So far as I can see, the duty of the Christy box can be raised still further until a practical limit is reached. This is what Prof. Christy has claimed all along; large quantity of solution treated in a small cubic space, but I can not up to the present indorse the economy of electrical power or electrochemical efficiency. I propose at some future date to repeat a rapid circulation experiment, such as the patent specification insists on, but the result of my No. 1 experiment and Scrymgeour's experience are not encouraging.

In the last month's experiments the cathodes (made of mill screening) received under the high-current density conditions a remarkably hard and bright deposit.

The following is a summary of the experiments made this month:

Experiment 4.—Speed of flow increased to 6 pounds per minute. Value before first circulation, 3.1 pennyweights; after first circulation (dip sample), 0.4 pennyweight; recovery, 87 per cent; duty, 96:1.

Value before second circulation, 0.88 pennyweight; after second circulation (dip sample), 0.34 pennyweight; recovery, 61 per cent; duty, 96:1. Total recovery, 90 per cent; duty, 96:1.

Experiment 5.—Current high, as in Nos. 3 and 4; speed of flow increased to 10 pounds per minute. Duty, 160 times capacity of box. Evolution of gas only apparent at lower end of box, and eventually, as current dropped, it had to be increased to maintain evolution of gas at electrodes. Value before first circulation, 5.4 pennyweights; after first circulation (dip sample), 1.2 pennyweights; recovery, 77.77 per cent; duty, 160:1.

Value before second circulation, 1.52 pennyweights; after second circulation (dip sample), 0.54 pennyweight; recovery, 64.51 per cent; duty, 160:1. Total recovery, 90 per cent; duty, 80:1.

Experiment 6.—Considering that the experiments summarized above were very satisfactory from the point of view of duty, percentage of recovery, but that the lowest values of solutions were 0.34 pennyweight (experiment 4) and 0.54 pennyweight (experiment 5), this experiment (No. 6) was made on solutions of low value, to determine the possibility of reducing solutions to the low gold values which obtain in our current practice here.

Current strength as high as in Nos. 3, 4, and 5, namely, 10 amperes.

Rate of flow of solution, 4 pounds per minute. Value before first circulation, lost in assay office; after first circulation (dip sample), 0.46 pennyweight; before second circulation, 0.62 pennyweight; after second circulation (dip sample), 0.12 pennyweight; recovery, 80.64 per cent; duty, 64:1.

Experiment 7.—Since this experiment (No. 6), was fairly successful, experiment 7 was made at a higher rate of flow (6 pounds per minute), and a lower density, 5 amperes, which showed an evolution of gas right through the experiment on the lower half of the set of electrodes. Value before first circulation, 0.5 pennyweight; after first circulation, 0.28 pennyweight; before second circulation, 0.52 pennyweight; after second circulation, 0.46 pennyweight.

This experiment I considered either salted, or incorrect, and the experiment was repeated.

Experiment 7a.—Evolution of gas profuse right through the experiment. Value before first circulation, 1.55 pennyweights; after first circulation, 0.44 pennyweight; before second circulation, 0.62 pennyweight; after second circulation, 0.78 pennyweight.

I have entered against this in my log book that the sample of second circulation must have been crossed; but now I believe that at the slow rate of flow of solution, the sample before circulation is incorrect, as the solution standing in the vats some 24 hours takes up more gold than the assay return shows.

Experiment 8.—Nos. 7 and 7a giving strong evolution of gas at comparatively low current, the rate of flow was increased to 6 pounds per minute. Results no good at all. Value before first circulation, 0.72 pennyweight; after first circulation, 0.54 pennyweight; value before second circulation, 0.56 pennyweight; after second circulation, 0.7 pennyweight.

Experiment 9.—Nos. 7, 7a, and 8 having given results of no value, No. 9 was made at the same rate of flow as No. 8, namely, 6 pounds per minute, and the current was increased to the strength used in No. 6, which gave a comparatively good result. Value before first circulation, 1.8 pennyweights; after first circulation (dip sample), 0.3 pennyweight; before second circulation (dip sample), (assay not done); after second circulation (dip sample), (assay not done).

I notice in one of your extracts from Prof. Christy's letters that he says he can reduce solutions to the value of 1 or 2 cents; but that he prefers to make it only 10 or 12 cents. This latter I have done in No. 6; but it is too high for our normal practice here, although the disadvantages might be outweighed (if it can not be overcome, which I do not believe) by the economy of initial outlay, efficiency, simplicity of clean-up, and other advantages inherent to the process.

DISCUSSION OF RESULTS.

In comment on the foregoing experiments, I can but express regret that old chlorination tanks had to be used. Evidences of the salting of the solutions at the most critical junctures are apparent. The omission of a record of the voltage and the amperage, hour by hour, of the duration of the experiment and of the volume of solution render it impossible to judge the ampere-hour efficiency. A two-barrel method of circulation is not satisfactory, for the reason that the velocity of flow diminishes with the diminishing head in the head tank, except when constantly regulated. The necessity of increasing the flow of solution as the liquid becomes impoverished of its gold and silver content can not be too positively emphasized.

It must be increased till the evolution of gas at the cathodes either ceases or becomes a minimum. Experimenters, by omitting these precautions, fail to obtain the results and the efficiency that are possible. It is true that gassing at the anodes need not be stopped, but some fail to appreciate the effect of the greater precipitating surface that I insist on. The best results are obtained by increasing simultaneously the cathode surface, the current density, and the speed of circulation. The current density should be kept at the highest point that will allow the metal to come down firmly coherent and to increase the circulation so as to reduce gassing at the cathodes to as low a point as is possible with the highest practicable current density. The limit of current density is reached when the metal comes down as a slime, and as it forms is washed off by the solution.

A difficulty that Andrioli must have met, though he does not mention it, was the intermittent use of the cathodes. From the dates of the experiments I observe that the interval was sufficient to cause the rusting of the iron wires beneath the gold. Some of the gold must have redissolved in the first part of his later experiments, and whether this was later corrected by the current can not be determined from the data given.

In Scrymgeour's experiments and Andrioli's first experiments the large amount of lime in the solution tested seems to have deterred them needlessly from employing adequate circulation. I have treated solutions rich in lime at velocities of flow of several feet per minute through gauze cathodes with no trouble from this source. With new cathodes trouble sometimes arises from a nonconducting coating of oil on the gauze or from the cathodes having been previously used and allowed to rust by intermittent use, as I believe was more probably the case.

I wish to express my hearty thanks to Messrs. Hopkins, Scrymgeour, and Andrioli for the trouble they have taken with these tests and my realization of the many limitations as to necessary conveniences and with constant interruptions. I consider the results favorable in view of the departure from the directions given and from the conditions that I would have desired.

SNODGRASS CYANIDATION APPARATUS.

A patent, of 10 claims, by J. Snodgrass (U. S. patent 835329, Nov. 6, 1906), appeared shortly after the experiments that have been described were made. The apparatus disclosed in the patent consists of a rectangular box through which the solution flows only once. The bottom of the box is covered with an iron plate, which is connected with the negative electrode. The cathodes are made of iron

frames resting on the bottom cathode plate, and either faced with iron-wire gauze of 100 meshes to the inch or with woven cloth of fine texture, coated with plumbago or with plumbago and a lead salt. The anodes are wooden boxes with coarse cloth sides, filled either with gas carbon or coke, graphite, binoxide of manganese, or peroxide of lead. The solution does not flow directly through the anodes, but is shunted around them. Carbons or other conductors are inserted into the box and connected with the positive pole. The iron plate connected with the cathode is claimed to have the advantage that any metallic powders falling on it from the cathode are prevented from being redissolved. The inventor expressly disclaims the use of rapid and repeated circulation of the solution through the deposition box, and urges this omission as an advantage.

It is apparent that effective precipitation under such conditions can be procured only by making the box large and costly and the clean-up difficult and expensive. To circulate the solution around and not through the anodes sacrifices one of the benefits of pervious electrodes. The iron plate at the bottom, on which the cathodes rest, is a good feature.

"COKE WHISKERS" AS AN ELECTRODE.

While I was engaged in a systematic search through all the known elements and compounds for a substance that would serve alternately as an anode and a cathode in cyanide solutions I received a specimen of the product popularly known as "coke whiskers." This substance was produced by Dr. J. A. Holmes in some of the experiments in coking coal that were undertaken by him at the Government testing plant at St. Louis, Mo.

The product closely resembles in size, shape, and color the hair of a negro's head. It is, however, a peculiarly resistant form of coke. It is but slightly attacked by the strongest nitric acid containing chlorate of potassium. It is a pervious mass, a good conductor of electricity, presents an enormous surface for deposition, and, in short, seemed to be the substance I had been looking for. It was not a newly discovered substance, but had been previously mentioned by Percy.^a He describes the substance as follows:

Hairlike form of coke.—Hairlike threads are sometimes observed on pieces of coke. They are nearly solid, and under the microscope occasionally present somewhat the appearance of a string of beads, soldered together. They consist of carbon, which seems to have been deposited in the following manner: A bubble of tarry or hydrocarbon vapor and gas, in escaping from the surface of the coke, becomes more highly heated, and is in consequence decomposed with

^a Percy, John, Metallurgy; fuel. 1875, p. 421.

the separation of solid carbon, which is deposited as a continuous coherent film on the surface of the bubble; a second bubble escapes through the carbonaceous shell of the first, and is similarly decomposed, forming a second carbonaceous shell attached to that resulting from the first bubble; and so, by a continuous succession of such deposits of carbon, a continuous tube of carbon is formed. Gas would continue to flow through this tube, depositing carbon in its course on the inner surface, until at length the tube is converted into a nearly solid fiber. Such appears to me the mode of formation of this curious hairlike matter, though I am by no means certain of the correctness of this view. I have noticed considerable variety in appearance in the specimens of hairlike coke, which I have examined under the microscope. This is a subject that deserves investigation by a competent microscopist.

From some accounts of the experiments at the testing plant at St. Louis I understand that few coals are capable of forming the product and that no one seems able to control the conditions that produce it. I tried to get quotations on the product in quantities. One coke manufacturer quoted it at \$20 per ton, but could not guarantee any quantity at that price. The subject, however, deserves further investigation, as there are many industrial uses to which such a material could be put.

EXCELSIOR CHARCOAL AS ELECTRODE.

The use of "coke whiskers" being out of the question on the large, commercial scale, I was forced to have resort to some other form of carbon that would be a substitute. It occurred to me that "excelsior fiber," a substance very generally used for packing and in the upholstering of cheap furniture, might be made into a pervious mass presenting a precipitating surface like zinc shavings.

Ordinary charcoal is practically a nonconductor, but I overcame the difficulty in this regard by heating the charcoal with metallic salts of silver, copper, or lead. I found that such charcoal could be converted into graphite in the electric furnace. Better still, I found that it was not necessary or even desirable to use the electric furnace, or to convert the excelsior entirely into graphite, as charcoal heated to a low orange became an excellent conductor without the addition of any foreign substance whatever. Grass, pine needles, straw, hemp rope, and many other materials also would serve, if coked at a sufficient temperature; but of all of these, excelsior charcoal proved the best. As regards ash content, for example, the excelsior was found to contain only about 1 to 3 per cent, whereas pine needles, for instance, often carry as much as 20 to 30 per cent.

I thus had a suitable material for pervious electrodes that could be used either as anodes or cathodes, or both in alternation. I found

that gold, silver, and copper could be precipitated upon such electrodes just as well as on a sheet of metal, and could be removed by making the charcoal cathode into an anode in a cyanide solution. The deposited metal could then be concentrated from a large cathode surface upon a small one. The most encouraging feature of all was that the charcoal of the anodes dissolved in the solution only at very high voltages, and after the gold and the silver had been removed. The action on the charcoal was much like that on graphite, and the charcoal, notwithstanding the large surface exposed, was less attacked than was hard carbon. Caustic lime seemed to precipitate any dissolved substance occasioning any discoloration; and after aeration, the solution so treated dissolved gold and silver as well as fresh solutions containing the same amount of cyanide would.

THE ELECTRODE SURFACE.

The area of surface exposed by "coke whiskers" and by excelsior charcoal is an important consideration. A cylindrical filament of "coke whiskers," 22 mm. long by 0.078 mm. in diameter and weighing 0.18 mg. has a skin surface, neglecting the area of the ends, of 5.388 square millimeters; therefore 1 gram of fiber represents an area of about 300 square centimeters. Thirteen grams of the material can be packed loosely, without difficulty, in a space of 384 cubic centimeters. Hence a gram occupies 30 cubic centimeters and has 300 square centimeters of precipitating surface.

"Excelsior charcoal" filaments may be produced of any degree of fineness. One average filament that I measured was 25 mm. long, 0.165 mm. thick, and 0.44 mm. broad. Its skin area would be 30.25 square millimeters, or 0.3025 square centimeters, and its weight was 1.6 mg. The surface of excelsior fiber thus may approximate 189 square centimeters per gram. The area for a given weight is then less than two-thirds that of an equal weight of "coke whiskers." Nevertheless "the excelsior charcoal," if made fine, is not so pervious to the solution, and on the whole works extremely well.

A comparison of the surface area of simple pervious electrodes as compared with the compound pervious electrode becomes of importance. When excelsior charcoal is placed in narrow rectangular boxes with cheesecloth sides to form electrodes that may stretch across the deposition box, two forms of construction are possible. If each box has a graphite or other conductor to supply the current we have what may be called a simple pervious electrode. If connected with the plus pole it becomes an anode, if connected with the minus

pole it becomes a cathode. Instead of making use of this arrangement, pervious anodes of another kind may be used. These may be graphite combs, perforated peroxide-of-lead sheets, or the peroxidized lead wire anodes previously described. Any combination of these makes a suitable working system. With the simple pervious cathode, having both sides exposed to an anode, the metal extends downward on both sides and penetrates the charcoal.

The simple pervious electrodes have given excellent results in the precipitation of metals from solutions, but have the disadvantage of requiring many electrical connections, one being required for each anode and for each cathode. As a consequence, whenever an anode or cathode is to be removed there is trouble in establishing and procuring the electrical connections. Constant watchfulness is then necessary to maintain good electrical contacts.

In figure 32 are shown two pervious cathodes, *c*, of the kind described. These may be supposed to be made either of wire cloth or of fragments of coke or graphite, or of "coke whiskers" or excelsior charcoal contained in a suitable box with sides of cheesecloth, and placed between pervious anodes, *a*. It would ordinarily be supposed that the whole of the inner surface of such pervious cathodes would be effective for receiving the precipitate of metal. However, I have found that metal precipitated by the electric current on such pervious cathodes forms a deposit of only moderate depth. The depth depends on the permeability of the material and increases with the free interstitial space. When granules of graphite, or of coke, one-eighth of an inch in diameter are placed in such frames, the metal deposit extends into the electrode to a depth of about 1 to 3 granules. With wire cloth it penetrates to a greater depth, but in all types, if the thickness of the electrode is great, the interior (marked *o*, fig. 32) receives practically no deposit, while the outer portions, marked with the minus sign (−), become heavily coated. The interior may be said, then, to be in an "electrolytic shadow." Here and in what follows regarding this neutral portion of the pervious electrode, I refer only to the metal that is deposited by the electric current, and not to that deposited by chemical action of the solution on the material of the electrode itself, as sometimes happens. The depth through which the current penetrates and acts on the solution varies from one-eighth to

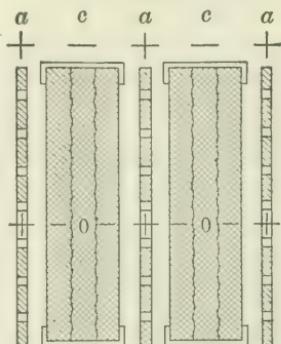


FIGURE 32.—Pervious electrodes. *a*, Anode; *c*, cathode.

one-half inch with the ordinary perviousness. The more compact the particles of the conducting substance, the shallower will be the metallic deposit, until at the extreme, when the perviousness diminishes to that of a sheet of compact metal, the deposit does not penetrate the cathode at all and is deposited on the surface. The discovery of this fact, which from the first appeared to be a disadvantage in the use of pervious cathodes, led me to simplify the pervious electrodes for receiving the deposit of metal. This feature is illustrated in figure 33.

In figure 33 is shown a deposition box, *A*, which is to contain the solution of a metal salt, such as copper sulphate, or cyanide of gold or silver and potassium. At *a'* is shown an insoluble anode of carbon or platinum, and at *c'* a cathode also of carbon or platinum. Now,

if there be placed in the solution between these anodes and cathodes a pervious electrode, made either of sheets of wire cloth or a mass of granules of coke, graphite, "coke whiskers" or "excelsior charcoal," and if an electric current be caused to enter the solution at the anode *a'*, and to pass out by the cathode *c'*, the end of the pervious electrode *c* nearest the anode *a'* becomes charged with negative electricity, as indicated by the minus sign, and copper or gold and silver will be deposited upon that side of the pervious electrode to a depth of one-eighth to one-half inch or more, depending upon the perviousness. The opposite side, indicated by the plus sign, of the pervious electrode becomes charged with positive electricity to a similar depth back from the face. The intermediate part, *b*, of the pervious electrode is neither negatively nor positively electrified; and practically no metal will be deposited there. My first improvement consisted in utilizing this idea in the construction of what may be called a compound pervious electrode. One face of this electrode acts as an anode and the other face as a cathode; between these faces is a part acting neither as a cathode nor as an anode, simply conducting the current as a solid metallic conductor would do.

Figure 34 shows the manner in which the compound pervious electrodes are used. Only the electrodes and not the deposition box are shown in this figure. The compound pervious electrodes are marked

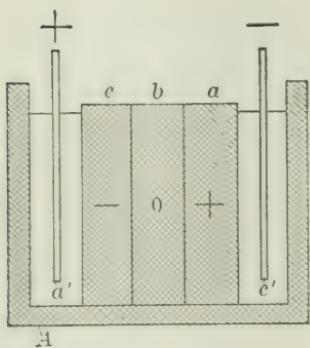


FIGURE 33.—Deposition box with pervious electrode. *a*, Anode (-); *b*, neutral part (0); *c*, cathode; *A*, deposition box.

e_1 and e_2 . They may be of any number desired. The positive electric current enters the solution by means of a simple pervious anode e , the whole of which becomes charged with positive electricity. At a suitable distance, preferably as small as possible without short-circuiting, is placed the compound pervious electrode marked e_1 . The side c nearest the anode e acts as a cathode and is marked with a minus (-) sign. The middle portion b is neutral and is marked o . The side a acts as an anode and is marked with a plus (+) sign. At a suitable distance is placed a second compound pervious electrode e_2 , and at proper distances as many more of these as may be necessary. Finally a simple pervious cathode e_3 , marked with a minus (-) sign, is provided where the electric current leaves the solution. The manner in which I prefer to arrange such a combination of compound pervious electrodes is shown in figure 35.

In figure 35, at B , is shown a large tank or reservoir containing the solution to be treated, and at A the deposition box. The solution is forced to circulate through the box A by means of the centrifugal pump F , driven by some such means as the motor G . The circulation is from the tank B through the deposition box, and back again repeatedly through pipe g . Also, solution may be drawn from the bottom of the tank and supplied to the tank on a float at the top, so that the poor solution above shall not mix with the rich solution below.

It is also possible to circulate the solution from the tank through the box once only, provided the box is made sufficiently long to insure complete precipitation in a single passage; but the method shown in figure 35 is preferable. The electric current enters at the simple pervious anode e , passes through the solution to the compound pervious electrode e_1 , then through the solution again to compound pervious electrode e_2 , and so on to the simple pervious cathode e_3 , by which it leaves the box through the ammeter E . At C is shown a suitable voltmeter for determining the voltage between the terminals of the deposition box A . By the action of the current each of the compound pervious electrodes e_1 , e_2 , etc., receives a metallic deposit on the side that is negatively electrified. The side a , as shown in figure 34, receives no metallic deposit and the part b practically none, unless by the chemical action of the electrode itself, while the side c receives the deposit as a whole. The part marked o being subjected to such action as occurs upon any anode, is liable to be attacked by

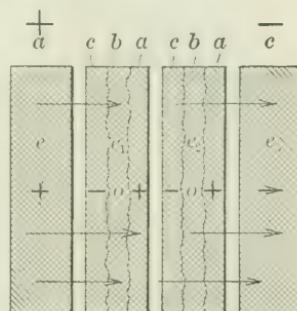


FIGURE 34.—Arrangement for compound electrodes. a , Anode (+); b , neutral part (o); c , cathode (-); e_1 , e_2 , compound pervious electrodes; e , simple pervious anode; e_3 , simple pervious cathode.

the solution unless made of some substance insoluble in the electrolyte.

In cyanide solutions "coke whiskers" and "excelsior charcoal" have been found sufficiently resistant to act as anodes at any ordinary voltage without protection. The aerated solution has the same solvent action upon gold and silver as does a pure solution of the same strength.

Such compound, pervious electrodes may also be termed pervious bipolar electrodes. They have a great advantage over the simple pervious cathodes. Thus a box requiring a potential drop of 2.5 volts with a 110-volt current can be arranged with 40 current gaps—

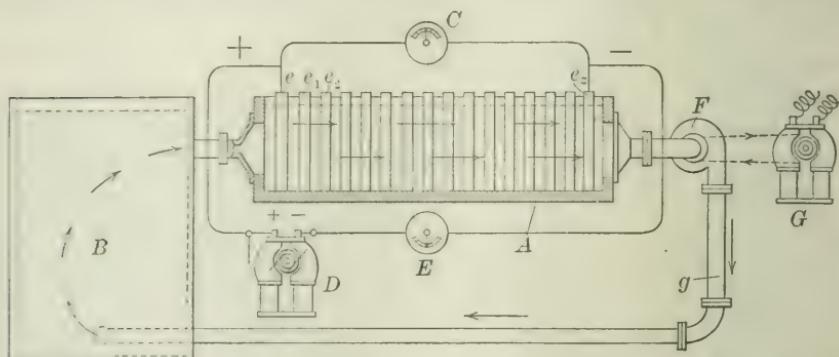
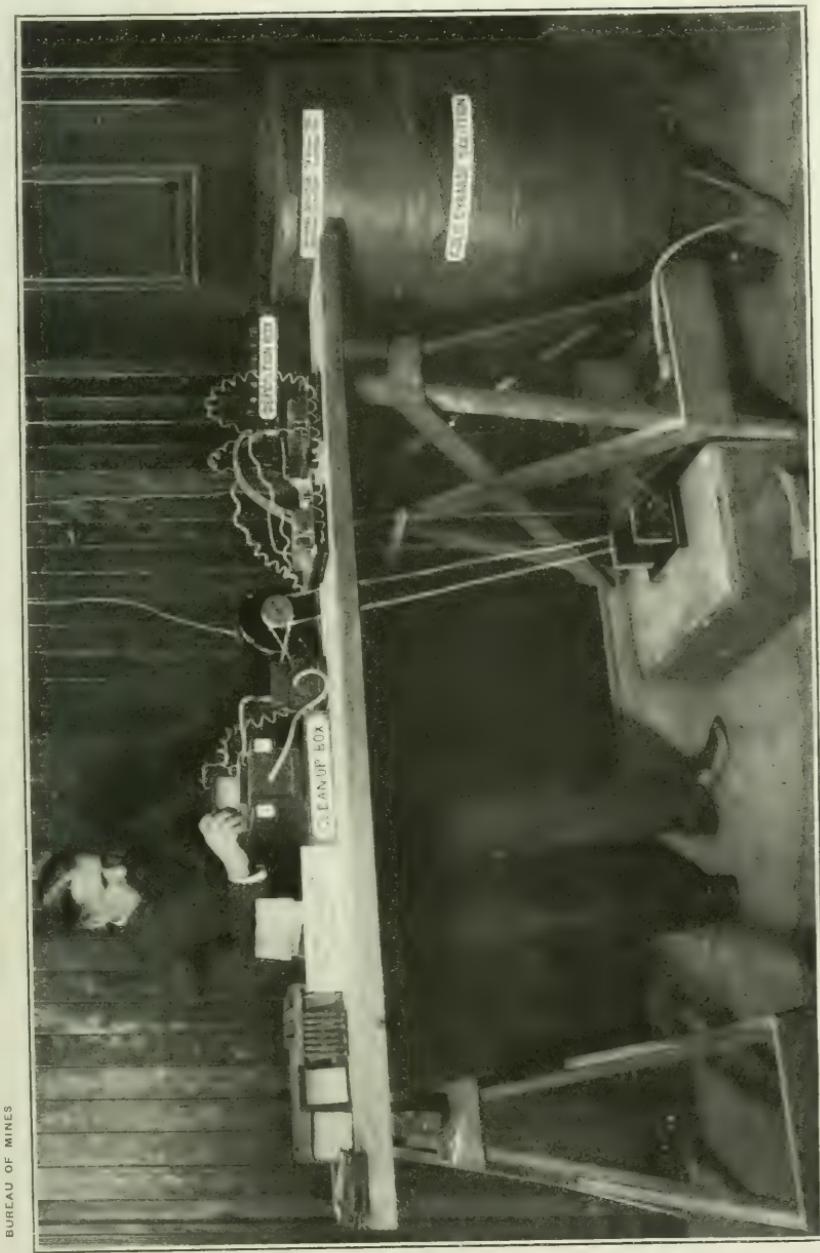
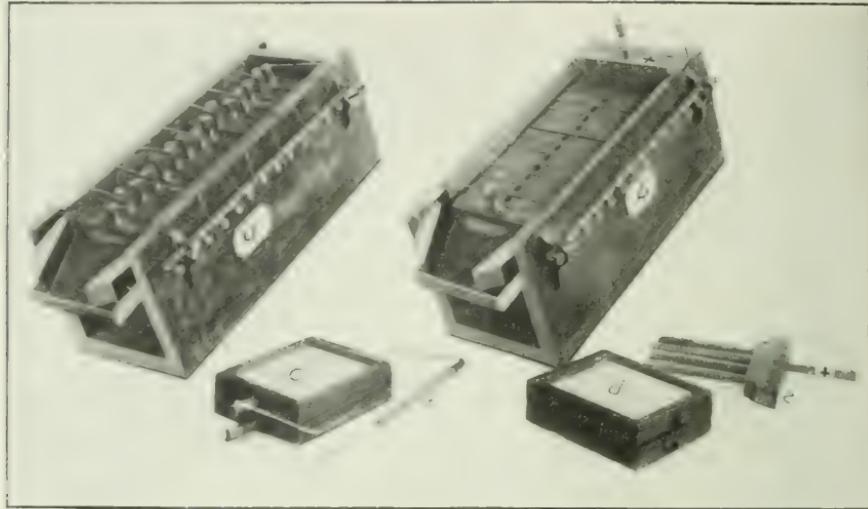


FIGURE 35.—Arrangement of apparatus for use with compound electrodes. e , Simple pervious anode; $e_1 e_2$, compound pervious cathode, and e_2 , simple pervious cathode. Other letters same as in figure 30.

namely, 1 pervious anode, 39 compound pervious electrodes, and 1 simple pervious cathode. There being only two electric connections to be made, any intervening compound pervious electrode can be removed and replaced as often as convenient without interrupting the current. If the simple pervious cathode at the end is to be removed, an uncharged one can be placed in front of it and connected with the negative pole, when the other can be removed from the circuit. A direct-current service of 220 volts has been used, but I do not recommend so high a voltage, on the whole, on account of the inconvenience to those working at the deposition box. It is, however, easy to protect one's self from shocks by wearing rubber-soled shoes, or, if necessary, rubber gloves. The 110-volt current gives no inconvenience without protection. A patent (U. S. patent 883170, Mar. 31, 1908) was granted me for the electrodes herein described, and further details may be found in the claims there set forth.

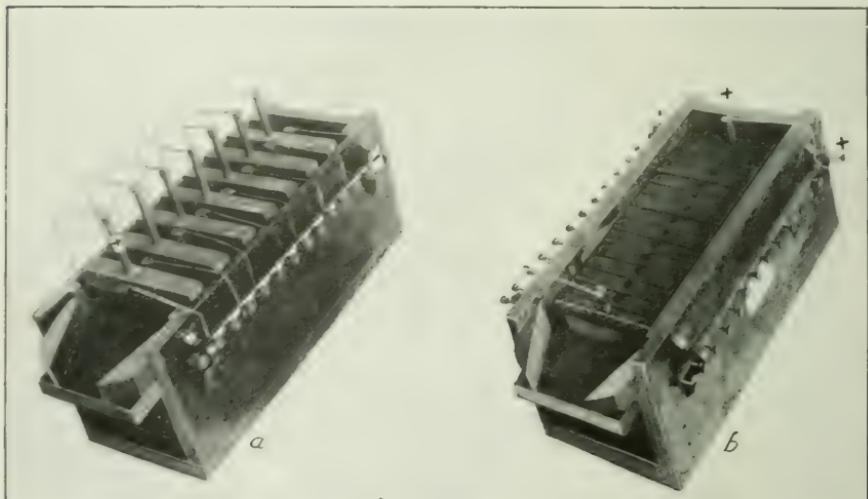


APPARATUS FOR ELECTRODEPOSITION OF GOLD AND SILVER FROM CYANIDE SOLUTIONS. CHRISTY PROCESS.



A. DEPOSITION BOX USED IN EXPERIMENTS.

a, Box equipped with 7 excelsior charcoal anodes and 8 charcoal cathodes; *b*, box equipped with 1 simple Acheson graphite anode (+), 13 compound charcoal cathodes, and 1 simple charcoal cathode; *c*, 2 simple electrodes; *d*, 2 compound electrodes; *e*, Acheson graphite anode; *f*, Acheson graphite rod $\frac{3}{8}$ inch thick.



B. DEPOSITION BOXES, ALTERNATIVE ARRANGEMENTS.

a, Box with 7 Acheson graphite comb anodes (+) and 8 simple excelsior charcoal cathodes (-); *b*, box with 1 simple charcoal anode (+), 13 compound charcoal cathodes, and 1 simple charcoal cathode.

DESCRIPTION OF AN EXPERIMENTAL PLANT.

As many readers may desire to verify the statements here made and to try the process on their own solutions, details are given here for complete small-scale tests. Such tests always should precede large-scale work, for by so doing the essential factors can be foreseen, and the necessary size of plant can be accurately determined. A type of plant used by the writer is shown in Plate I.

DEPOSITION BOX.

The early experiments were made with a box 10 inches in length, which afterwards was increased to 13 inches, as shown in the illustrations, and still later to several feet. The box is 6 inches deep and $4\frac{3}{4}$ inches wide and discharges at a height of $4\frac{1}{2}$ inches. It is illustrated in Plate II, A.

The box is made of redwood 1 inch thick. The end joints are put in with a tenon and two pieces of string are laid along the joints to bruise the wood, causing it to swell tight when wet. After being nailed, the box is immersed in water until it swells tight. It is then taken out and partly dried, after which it is given several coats of a special paint, such as "P & B" paint made from residues of California petroleum dissolved in carbon bisulphide. It is important not to apply the paint until the wood has swelled. If painted first, the box can never be made tight. Boxes fitted with circular-saw joints leak less, as a rule, than those with planed joints.

ELECTRODE BOXES.

The electrode boxes are made of strips of soft wood one-half inch thick and three-eighths inch wide. On the bottom is nailed a strip one-eighth inch thick and three-fourths inch wide. These are fastened together, and over the rear side is stretched a piece of cheesecloth, which is drawn tight, overlapping, and fastened to the box with thick "P & B" paint.

The outside dimensions of the frames as constructed are $4\frac{1}{2}$ inches wide by $5\frac{1}{4}$ inches high. The inside dimensions are $3\frac{13}{16}$ inches wide by $4\frac{5}{16}$ inches high. The box is half an inch deep. The inner cross section is practically 16 square inches or 1 square decimeter; that is, one-ninth square foot or 0.01 square meter. For making a new apparatus I should advise an inner cross section of 4 by 4 inches, making exactly one-ninth square foot, or 1 square decimeter, and should modify the dimensions of the deposition box accordingly.

The cover of these boxes is made three-eighths inch wide and one-fourth inch thick. Stretched over the inside and lapped over the outside is a layer of cheesecloth, which is fastened to the frame by a

coat of thick "P & B" paint. The cover is provided with a small pin at the bottom to be inserted in the projecting lip at the bottom of the frame, and is fastened on the top by a simple clamp made of hard rubber. The box, when thus made and assembled, holds approximately 8 to 10 grams of excelsior charcoal in a space 10 by 10 by 1.25 cm. in size. The box should be put together in such a manner that the cheesecloth side of the cover is in direct contact with the charcoal, thus leaving a space of one-fourth inch between the several boxes.

When these boxes are used as compound pervious electrodes they require no further addition, but when it is desired to use them for simple pervious cathodes an aperture of about one-fourth inch through the center of the box at the top is necessary for the introduction of the electrode rod of Acheson graphite. For simple pervious cathodes, however, a wire of iron, silver, or copper may be used, but the graphite rod is preferable. As thus constructed and assembled the box has a thickness of about three-fourths of an inch. Allowing for slight irregularities in construction, it is possible to use 15 of these boxes in a distance of 1 foot in length of the box; and as 1 of these serves as an anode, there are 14 effective compound pervious electrodes in each foot of length of box. Formerly I so made these boxes as to contain a layer of charcoal an inch thick, but found that better results could be obtained by reducing the thickness to one-half inch. Beyond this limit it does not seem to be wise to go. With the compound pervious electrode it is necessary to pack the charcoal as thick as indicated, namely, at least 10 grams to each box, to prevent passage through the charcoal without full chemical action. With two such boxes as I have indicated here—that is, with 28 current gaps—I have employed a voltage of 110.

CIRCULATING PUMP.

In order to give a small, compact precipitation plant, the use of a centrifugal or other circulating pump is necessary. The pump used in the small-scale experiments has been already described. For packing the stuffing boxes I use a little cotton or wool soaked in graphite and vaseline. The whole interior of the pump is painted with "P & B" paint, and where thus protected shows no signs of wear or chemical action. The only part of the pump which is not thus painted is the shaft, which is kept bright by the graphite and vaseline. I use two pumps on the same bedplate in preference to one in order to balance the side thrust.

The deposition box that I have here described has 4.28 liters capacity up to the water line. When filled with 15 electrode boxes with their charcoal content the clear space is about 2.4 liters. If the

compound pervious electrodes are not used, I prefer to use anodes made of Acheson graphite or the wire ones of peroxidized lead. In the small box are four Acheson-graphite rods about three-eights of an inch in diameter. The upper ends of these are inserted in a graphite bus bar having conical or threaded holes an inch apart, thus giving an anode of comb-shaped form. I have used these graphite anodes repeatedly at 4 volts without signs of disintegration.

With simple pervious anodes I place an anode on either side of a cathode or between each pair of cathodes. With solutions containing sulphates I prefer to use the peroxidized-lead wire anode described on page 100. In this case I use a square frame made of painted wood three-fourths inch wide and one-fourth inch thick. Through this are stretched six lead wires about one-eighth inch in diameter, coated with peroxide of lead in the manner described. The wooden frame is coated with "P & B" paint.

In assembling the apparatus I connect the two suction pipes of the double pump at the opposite sides of the solution tank, preferably from near the bottom, rather than from the top, as in figure 35. The pump discharges through the deposition box, and the solution returns on the float board at the top of the tank, avoiding admixture with the stronger solution below. The circulation is maintained until the gold and silver content of the solution is sufficiently reduced.

I find the unit deposition box that I have described very convenient for use. The length of the box may be increased, if desired, or the same result may be attained by placing one box behind another, in series, until sufficient precipitating surface is obtained. With rich solutions containing much gold and silver, I have had the silver deposit so fast as to clog the filter cloth, a growth of silver having been formed on the outside of the cover, necessitating the removal of this from time to time to clear away the crystals of pure silver. This does not happen with poor solutions. However, as the interstitial space of the electrodes becomes filled with gold and silver, and particularly if the solution is foul with lime and ferrocyanide of potassium, often there is a considerable resistance to the circulation of the solution. There are two remedies for this, one is to reduce the speed of flow and the other to increase the grade of the box. I have frequently in precipitating rich solutions, on this account, inclined the box 1 to 1½ inches to the foot, and have experimented with velocities of flow ranging from 2 to 5 liters per minute in the box of the size indicated. If the actual interstitial space in the box is about 2½ liters, the actual rate of flow through the box would be 1 to 2 feet per minute. Such a rate, however, is not necessary with rich solutions. It will be noted in the foregoing that even greater velocities of flow may be required with dense currents and

low metallic content of solution to obtain rapid precipitation. When, toward the end, the solution becomes much reduced in metal the charcoal becomes choked with hydrogen bubbles, and the grade of the box must be increased or, with a high rate of circulation, the box will overflow.

DISTRIBUTION OF PRECIPITATION IN THE DIFFERENT CELLS.

When simple pervious anodes and cathodes are used, there is a uniform voltage throughout the whole deposition box, and the metal is precipitated on the outer side of each cathode uniformly throughout the box. With compound pervious electrodes a uniform distribution of voltage can be obtained if the charcoal is carefully packed so as not to leave any clear path for the electric current through the solution and not through the charcoal. There is always a tendency for the charcoal to settle in the box, and there is frequently a clear passage for the current along the water line or along the edges of the frame. In order to prevent this, care should be taken in packing the boxes. Moreover, electrode cells may be staggered by wedging them close to alternate sides of the deposition box, although it is preferable to avoid such grooves in a small experimental box, as they complicate cleaning in preliminary tests. In large boxes grooves are, of course, necessary. With proper precautions taken, the fall of voltage is very uniformly distributed throughout the box; but there is nearly always a tendency for the difference of potential between the first two boxes and the last two boxes to be greater than between the others. If the boxes are carelessly packed the difference may be considerable. On this account the first anode in the compound pervious electrode box should be a graphite comb or of peroxidized-lead wires. This distributes the current uniformly across the whole section of the box, and somewhat reduces the resistance.

If the distribution of the voltage throughout the box is uniform and the circulation of the solution through all parts of the box is also uniform, the precipitation of gold and silver will be very uniform. With the compound pervious electrodes the coating of silver seldom is more than one-eighth to three-sixteenths or at most one-fourth inch thick, but there is always a tendency for the simple pervious cathode at the end of the box to become more thoroughly coated than the others, owing to the leakage of current from the upper electrodes. For this reason it is good policy in treating very rich solutions to replace the last simple pervious electrode at the end of the box, as it becomes charged with silver and gold, more frequently than the others. The compound pervious electrodes also should be examined at intervals, and if the metallic precipitate tends

to creep up on the outside of the cover, giving danger of short-circuiting, it is best to remove the covers, replace them with fresh ones, and when convenient remove the silver from the coated covers. If desired the metal-laden charcoal may be replaced continuously, for no harm is done if any one of the compound pervious electrodes is removed from the series and replaced by another with fresh charcoal.

The experimental deposition box shown in Plate II, *A*, I have found most convenient. Boxes *a* and *b* are of the same dimensions and, as has been described, are 13 inches long on the inside and are capable of holding 12 inches of electrodes, allowing three-fourths inch for the distribution of the incoming solution at the head of the box and one-fourth inch for the discharge at the tail end. Box *a* is shown mounted with one form of simple pervious electrodes. There are seven simple pervious cathodes filled with excelsior charcoal and eight simple pervious excelsior-charcoal anodes. Each box is provided with an Acheson-graphite rod for the distribution of the current from the bus bar, the anodes being connected with a positive bus bar, and the cathodes with a negative one. At *c* are shown two of the simple pervious cathodes, one directly beneath the other. The only difference between the simple pervious anodes and the corresponding cathodes in this form of construction lies in the one being connected with the positive current and the other with the negative. At *d* are shown two of the same boxes used as compound pervious electrodes, the difference being that the electrodes *c* are provided with graphite rods for connecting them with the bus bar, whereas electrodes *d* require no such provision. However, as the simple pervious cathode has silver deposited on either side of the cloth, such cathodes are more convenient when made with a rectangular frame for the box one-half inch thick and with two covers one-fourth inch thick, provided with cheesecloth backing, so that the covers may be removed from either face of the electrode for removal of the charcoal. This construction is not absolutely necessary, but it makes the clean-up more convenient.

The box *b* shows the arrangement for a number of compound pervious electrodes and is the form that I prefer for that kind of work. At the head of the box, marked with a plus (+) sign, is shown the Acheson-graphite anode by means of which the positive current is introduced into the solution. This anode, shown at *e*, may be termed the Acheson-graphite comb anode. It consists of a bus bar of Acheson graphite into which are inserted four graphite rods, clamped together by means of graphite screws. The material is entirely of graphite except the little brass cap to which is fastened the copper connecting wire. The advantage of the Acheson-graphite anode is

that it more thoroughly distributes the current over the whole cross section of the box than would excelsior charcoal alone. As has been said, instead of the Acheson-graphite anode the peroxidized-lead wire anode may be used and is preferable if sulphates are present. In any event the intervening compound pervious electrodes *d* remain unchanged.

These boxes are as compact a form of construction as I have been able to devise of this type. In each box the solution is introduced into the box by the centrifugal pump, flows through the pervious electrodes, and out of the box again into the main tank. It will, of course, be understood that the grade of the box as shown in Plate II, *A*, is for convenience in representation. The grade that I prefer to use is about 1 to 1½ inches to the foot.

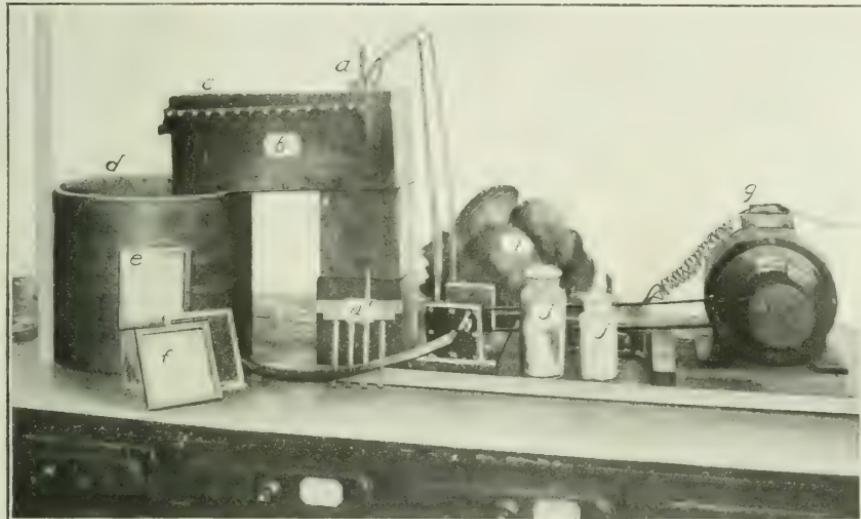
Alternative arrangements are shown in Plate II, *B*. At *a* is shown a very satisfactory form of simple pervious electrode, having seven simple, pervious, Acheson-graphite comb anodes and eight simple, pervious, excelsior-charcoal cathodes similar to *c*, Plate II, *A*, the cathodes being all connected with the negative bus bar and the anodes similarly connected to the positive bus bar.

The simple pervious electrodes shown at *a* in Plate II, *B*, are on the whole preferable to those at *a* in Plate II, *A*, as the anodes of graphite are less acted upon than those of charcoal. The graphite anodes may, of course, be replaced by those of peroxidized-lead wire.

An alternative form of compound pervious electrode is shown at *b* in Plate II, *B*. The current here enters the simple pervious anode marked with a plus (+) sign, passes through the 13 compound pervious excelsior-charcoal electrodes and out through the simple pervious cathode, marked with a minus (—) sign at the lower end of the box. As the simple pervious excelsior-charcoal anode is not so good a conductor as the Acheson-graphite or the peroxidized-lead-wire anode, it does not so evenly distribute the current across the head of the box, and, as stated, I prefer the Acheson-graphite comb anode or the peroxidized-lead wire.

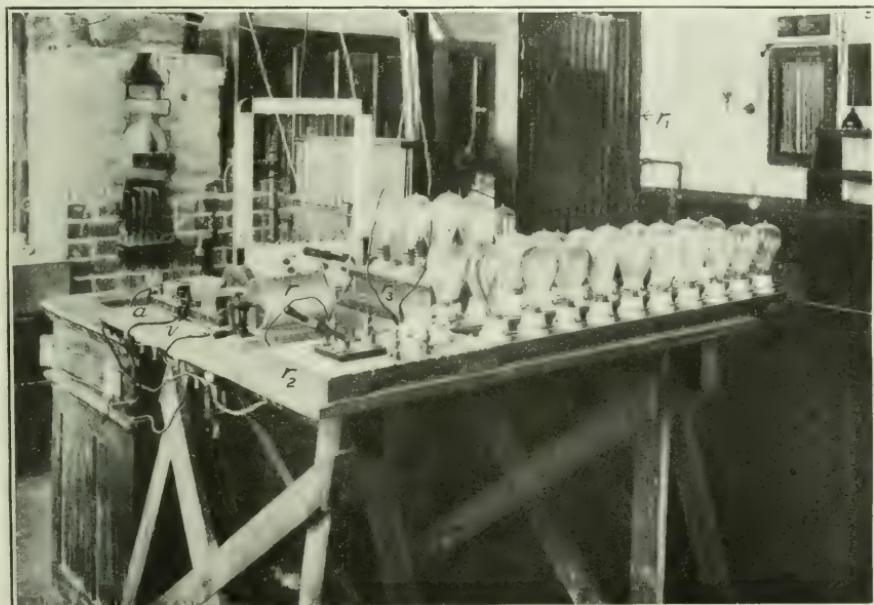
Plate III, *A*, shows the apparatus equipped with the compound pervious electrodes such as was used to handle a 20-liter charge. The box, *b*, is of 4.28 liters capacity, and, with the electrodes, 2.4 liters. The box, together with the tank *d*, holds 22 liters of solution, a convenient charge for an experiment.

The positive current passes to the Acheson-graphite anode *a*, thence through the compound pervious electrodes, not shown, and out through the simple pervious cathode, *c*. The solution overflows from the box into the tank and then passes through the two pumps, *h*, and back again through the box, circulating until the extraction is completed. The motor, *g*, shown here for operating the pump is needlessly large. A compound pervious electrode box ready for use

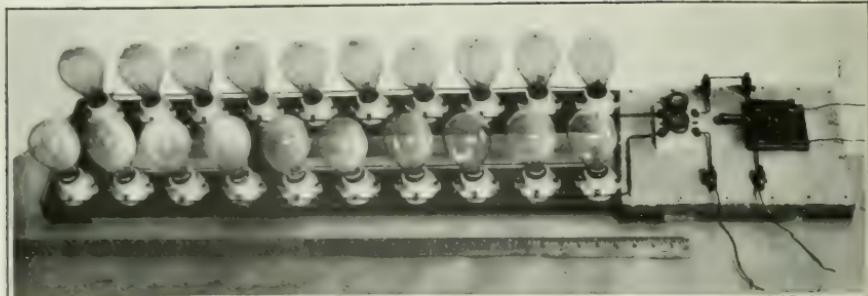


A. WORKING MODEL. CHRISTY PROCESS.

a, Acheson graphite anode; *b*, deposition box; *c*, simple charcoal cathode; *d*, solution tank; *e*, compound electrode holder; *f*, cover of holder; *g*, motor; *h*, pump; *i*, excelsior charcoal; *j*, bottles of silver residue.

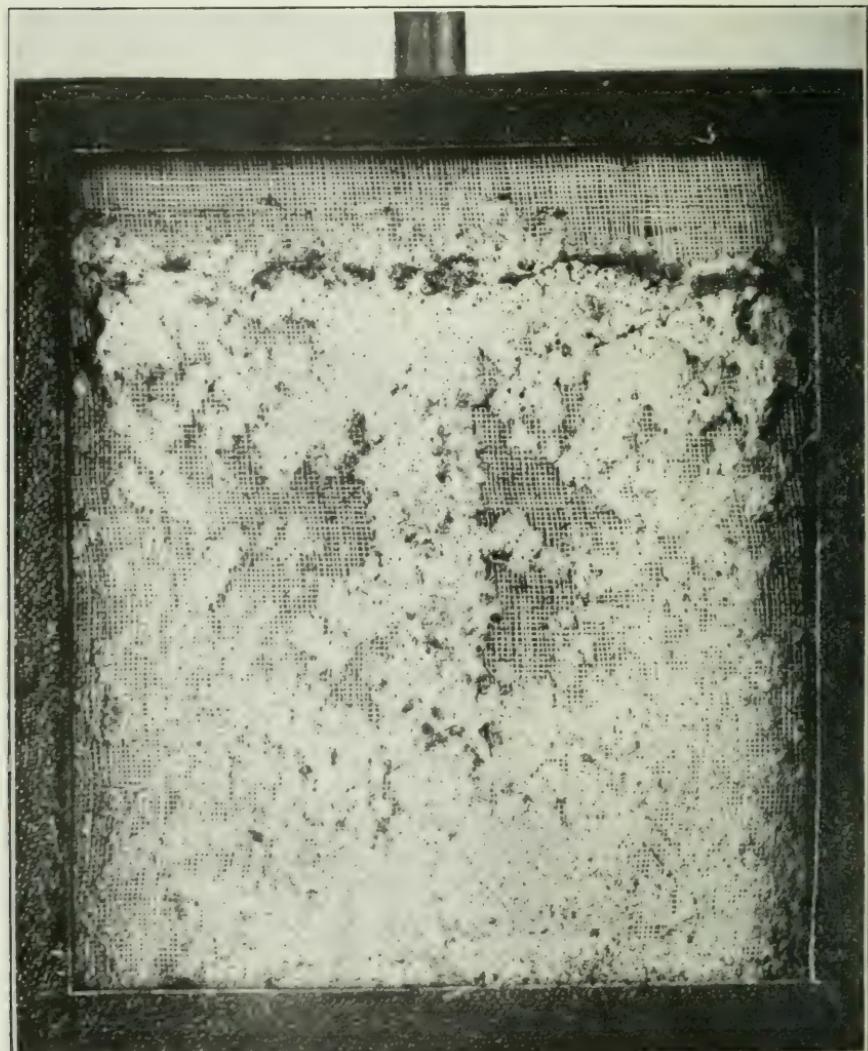


B. BANK OF LAMPS USED FOR RESISTANCE.



A. CONVENIENT RESISTANCE FOR EXPERIMENTAL WORK.

20 lamps in parallel, either 8, 16, or 20 candlepower as desired. Any number may be cut out as needed.



B. PERVERS CHARCOAL CATHODE, SHOWING CRYSTALS OF FINE SILVER ON CHEESEECLOTH FRONT COVER.

is shown at *c*. At *f* is the cover of a compound pervious electrode, and behind this is seen the box itself filled with excelsior charcoal ready for use. The Acheson-graphite anode is shown at *a*. In the rear of the apparatus is a pan filled with excelsior charcoal as it comes from the retort. The two bottles, *j*, in the foreground contain silver residues from the clean up and show the material as it appears after roasting.

Plate III, *B*, from a photograph taken in the old mining building at the University of California, shows the means of regulating the current. The laboratory is provided with a 110-volt direct current from a storage battery or from a dynamo. This current is brought into the laboratory at *a*, the main current passing through the resistances r_1 , r_2 , and r_3 . By connecting with varying points on this resistance, a shunt is formed with any desired voltage for the deposition box. The shunt current passes the ammeter *a* and the small adjustable resistance r and through the deposition box and back again to the resistance. A voltmeter to terminals of box is shown at *c*. The resistance r is used for adjusting the voltage accurately. By this means a slight waste of current results in the experiment, it is true, but it is possible to get any voltage needed from 110 volts to 1.

The system shown was resorted to after many experiments with small special dynamos, storage batteries, and other devices, and enables one to make use of a 110-volt direct current with no inconvenience. Moreover, by the means shown it is possible to regulate the voltage to 0.1 volt and keep it steady all day if necessary. It is necessary only to change the point of application of the shunt or throw in or out a few coils in r_1 or throw in or out a few of the lamps in the resistances r_2 , r_3 , making the final adjustments by the resistance r .

Plate IV, *A*, shows in detail the arrangement of a suitable shunt resistance. The frame carries 20 sockets, in which may be inserted in parallel electric-light bulbs of any desired candlepower supplying the resistance. These resistances are convenient and they are used generally about the laboratory.

MODE OF CHARGING THE BOXES WITH EXCELSIOR CHARCOAL.

The charcoal as it comes from the retorts is in the form of large ball-like masses of closely interlocked fragments. I loosen up the shreds of charcoal carefully so as to reduce the breakage to a minimum and form a mass of homogeneous threads. The material is then carefully charged into the boxes. In order that the charging may be uniform I prefer to counterpoise the box on a weighing scale and to add the charcoal until the required weight is obtained. With

compound pervious electrodes I prefer about 5 pounds of charcoal to the cubic foot of cathode space, and for simple pervious electrodes about $2\frac{1}{2}$ to 3 pounds. As I have already stated, the fine charcoal is put at the back or the anode side of the compound pervious electrodes, care being used to fill the box so that no clear space is left for a direct passage of the current. This is particularly necessary with the compound pervious electrodes, the aim being to pack it so that on being held up to the light no light is seen. When so packed the "electrical shadow" or neutral part will also be complete. This leaves 80 to 90 per cent of the interior of the box for solution and deposited metal. The material should be packed a little harder along the edges than in the middle. An inner diaphragm, mentioned in the S. B. Christy patent specifications, I have found unnecessary, provided the charcoal is carefully packed along the edges. A little "P & B" paint at the edges of the cheesecloth prevents electric leakage at these places.

PERMANENCE OF EXCELSIOR CHARCOAL.

If the excelsior charcoal is burned at an orange heat for an hour after the escape of gas ceases it has a steel-blue color, and I find that in this condition it is very little acted upon by the current even when used as an anode. So long as the silver and the gold are contained in the solution the charcoal is acted upon only in the very slightest degree; but after the gold and the silver have been precipitated, particularly if much caustic potash is present in the solution, the charcoal is attacked at a high voltage and slowly imparts to the solution a slight color like that of very weak tea. This coloring matter can be entirely removed from the solution by quicklime, but such removal is not necessary. I have found the action of the solution to be unimpaired if the solution is thoroughly aerated before being used as a solvent for gold or silver.

DETAILS AND RESULTS OF TESTS.

To leave no doubt as to the possibilities of the process I shall go somewhat into detail in certain experiments made by me on various gold and silver bearing solutions. The form of tables which I have adopted I believe to be the briefest and clearest. The conditions as to the circulation of the solution are not always specified, but it should be understood that the rate has usually been 1 foot per minute. In some tests a lower velocity has been found to suffice with solutions very rich in gold and silver, but with an impoverished solution it is well to increase the circulation to the rate specified to attain a satisfactory rate of precipitation.

The capacity of the boxes containing the charcoal electrodes is not quite so great as of those containing the wire-gauze electrodes. On account of the permanence of the charcoal, however, in first experiments it is better to treat charges of 20 liters at a time until familiar with the manipulations. Results can be obtained then in a single day's work and samples taken in the uninterrupted course of the precipitation. Before large-scale work is begun I should recommend charges of about 500 liters per day, and continuous operation. In this event samples need not be taken so often; perhaps once in four to six hours will suffice. The rise in cyanide content when rich silver ores are being treated will not be as rapid as in the small-scale work, for the reason that the large volume of solution treated requires a longer time for extraction. The rate of increase ought to be inversely proportional to the volume of solution.

In treating ores containing much silver it is not necessary to assay continuously, for if a sample of 1 c. c. of the solution is taken, and to it is added 1 c. c. of dilute sulphuric acid a precipitate of cyanide of silver shows silver to be still present in the solution to the amount of 4 to 5 mg. per 100 c. c. From the density of this precipitate the silver content can be closely estimated by eye. The rate of precipitation, in treating rich silver ores, can also be determined, if the voltage is uniform, by the fall of amperage. So long as the silver is present the current will be high, but as soon as the silver content of the solution falls the current also falls. As regards silver, results plotted on cross-section paper clearly indicate, by the form of the ampere curve, the point where the silver is substantially removed. With gold solutions this does not apply so strictly. The most economical point to stop precipitation is after the cyanide content ceases to increase and begins to decrease. I strongly recommend the plotting on cross-section paper of results obtained in all experiments. Such representation shows the facts in a striking manner and gives a better idea than can be obtained by examining numerals.

TAKING SAMPLES.

For ordinarily rich solutions 100 c. c. portions of solution have been used as samples. The sample is evaporated in a lead boat at a gentle heat with a good but not a strong draft. The evaporation takes place in an hour. The ears of the boat must not be folded tight or capillarity will cause the solution to climb and dry on the sides of the boat, leading to mechanical losses and low results. The dried residue in the boat is sprinkled with a little boracic acid, scorified, cupelled, and parted in the ordinary way. For very low grade gold solutions I prefer to take 603 c. c. of solution for evaporation, and, after scorifying, cupelling, and parting, to weigh the button of

gold in milligrams. Then every milligram represents \$1 in gold per ton of solution, and the amount is obtained directly in dollars and cents. This weight of 603, or more accurately 602.9 grams or approximately 602.9 c. c. of solution, I call the "California gold ton." With low-grade solutions a liter sample may be desired.

I always prefer the evaporation of the solution to any other method in use, as it is absolutely reliable if care is taken to avoid mechanical loss. With 100 c. c. samples results are obtained in about 2 hours. The evaporation method is to be preferred, but the following method of assaying cyanide solutions is satisfactory also, except for solutions very rich in cyanide:

To 100 c. c. of cyanide solution add 6 to 7 c. c. of a 10 per cent lead acetate solution, then add 3 grams of zinc shavings, heat just short of boiling, add 200 c. c. of strong hydrochloric acid, and heat again just below boiling so as not to break up the lead sponge which forms. When the zinc has been nearly dissolved, remove the precipitate of spongy lead, squeeze as dry as possible upon a piece of test lead, dry gently upon the hot plate, wrap with the test lead into the form of a ball and place upon the cupel. The time required to prepare the sample for the cupellation is 15 to 20 minutes. This method, suggested to me by Mr. F. J. Buel, I have found to be particularly satisfactory for solutions poor in gold and silver and not too high in cyanide. When there is a large amount of free cyanide present the results are sometimes low. Where the gold and silver content of the solution is very low and it is difficult to recover the gold bead, which is sometimes very small, it is sometimes an advantage to add 1 c. c. or more of a standard silver nitrate solution before precipitation. The silver nitrate will be precipitated on the lead and add to the size of the bead, preventing loss on cupellation. If desired to estimate the silver, one can deduct the value of the silver nitrate added.

USE OF AMMETERS AND VOLTMETERS.

It is absolutely impossible to do any satisfactory work with electrical precipitation without having constantly in the circuit a reliable ammeter and a voltmeter at the terminals of the cell. It is absolutely necessary to know what amount of current is passing through the solution. When these instruments are used, short circuits are instantly detected by the fall of potential and the rise in amperes, and it is desirable to record these results, as I have done, to know what is happening.

ADVANTAGE OF USING METRIC VALUES.

In investigations of this sort it is important to express results in simple form and to arrange the simultaneous variables in commen-

surate units. The metallurgy of the precious metals has been greatly retarded by the antiquated method of reporting gold and silver in ounces, pennyweights, and grains Troy, with other variables in pounds avoirdupois or in that uncertain unit, the ton, which may mean either the short ton of 2,000, the long ton of 2,240, or the metric ton of 2,204.6 pounds. The American custom of reporting gold in dollars and cents is not much better, for there is always the uncertainty as to whether the silver has been figured at variable current prices, or at one dollar an ounce. The natural difficulties of the problem are numerous enough. No one who has endeavored to correlate work done in Korea, Australia, South Africa, Mexico, South America, and the various American regions can fail to desire the elimination of all complexity possible.

The use of the metric system, estimating large values in metric tons of 1,000 kilograms, and small values in kilograms, grains, or milligrams, has an enormous advantage. Values for volumes and specific gravities are easily converted into definite weights without the uncertainties of the various incommensurate English units. For instance, if gold and silver are reported in milligrams per 100 c. c. of solution, ten times that number gives the number of milligrams per liter (practically per kilogram) and the number is at once the number of grams of gold and silver per metric ton of solution.

If the milligram weight of gold per 100 c. c. is multiplied by \$6.03 we have approximately the assay value of the gold solution per ton in dollars and cents. If the milligram weight per 100 c. c. of either gold or silver be multiplied by 0.29166+, the number of ounces per ton of 2,000 pounds will result. Or, if we multiply by 0.3 we have the approximate number of ounces of metal per ton of solution.

Of these methods of expressing values, the most useful is the expression of grams of gold and silver per metric ton of solution. This method, already widely used in Mexico and in most Spanish-American countries, is much more rational than the one used in this country.

IS COMMERCIAL CHARCOAL SATISFACTORY FOR PERVERS ELECTRODES?

In order to settle this point, commercial oak charcoal, used in the laboratory as fuel, was tested with 50 volts. No spark resulted and no current passed as measured by a milliammeter. One piece only that had evidently been overheated showed a trace of a spark at 50 volts. This piece was rejected and the remaining 74 grams was crushed to between 6 and 8 mesh size and filled into a box having cheesecloth sides. This was made a cathode by inserting a graphite rod connected with the negative pole. One graphite comb anode was used. Three liters of a cyanide of silver solution with 0.1 per cent

KCy and 0.1 per cent KHO were then circulated through the box for six hours, with the following results:

Results of test with oak-charcoal cathode.

Time, hours.	Volts.	Ampere.	Silver, mg. per 100 c. c.
0.....	3.5	0.060	126.64
3.....	3.5	.055	119.72
5.....	3.5	.082	106.02

This experiment proved beyond a doubt that such charcoal was practically a nonconductor. The silver did not precipitate on the charcoal, to any perceptible extent, but came down firmly on the graphite conducting rod, and collected slightly between the grains of charcoal. There may have been some chemical action by the charcoal, but none was visible, it came out as black as when it went in. The charcoal not only did not help but actually hindered and acted as would so much nonconducting sand adding to the electric resistance.

RESULTS OF TEST WITH EXCELSIOR CHARCOAL CATHODES.

Three liters of 0.1 per cent KCy solution containing 0.1 per cent KHO, was treated with a single previous cathode of 10 grams of excelsior charcoal, which had been ignited at a low yellow heat. The solution was not as strong as had been used before, but all other conditions were similar. The results were as follows:

Results of test with excelsior-charcoal cathodes.

Time, hours.	Volts.	Ampere.	KCy content, per cent.	Silver, mg. per 100 c. c.
0.....	3.5	0.275	0.097	74.36
1.....	3.5	.320	.1055
2.....	3.5	.360	.1195
3 $\frac{1}{2}$	3.5	.285	.1430	.32
4.....	3.5	.258	.138	.10
6.....	3.5	.249	.111	.05

The precipitation was practically complete in four hours, which is in decided contrast with the results shown of the previous experiment. The high current with the low voltage was due to the high electrical conductivity of the excelsior charcoal.

TO WHAT EXTENT DOES EXCELSIOR CHARCOAL ALONE PRECIPITATE SILVER?

In this experiment 3.3 liters of 0.1 per cent KCy solution, containing 0.1 per cent KHO, were circulated through 14 grams of excelsior

charcoal with no electric current passing. The results were as follows:

Results of test with excelsior-charcoal cathode and no electric current.

Time, hours.	Volt.	Ampere.	KCy con- tent, per cent.	Silver, mg. per 100 c.c.
0	0	0	0.0995	124.40
2	0	0	.0965	122.64
4	0	0	.0945	120.78
5½	0	0	.0935	119.84
9½	0	0	.0935	110.86

The 14 grams of excelsior charcoal had precipitated about 1 per cent of its own weight of silver. The loss of cyanide was small and no regeneration occurred as in the experiment in which electric current was employed.

LOSS OF CYANIDE ON CIRCULATING THE SOLUTION.

Following the previous investigation, experiments were undertaken to ascertain whether a loss of cyanide occurred from circulating the solution with the centrifugal pump. It was found that no such loss took place in the circulating solution when no electric current was passing, provided protective alkali was present, but that with no alkali a slight loss of cyanide occurred in eight hours, evidently due to the presence of carbonic acid from the air.

The cyanide titration each hour gave the following results:

Results of test for cyanide loss from circulation.

	Cyanide, per cent.
Beginning of test	0.1
End of first hour	.099
End of second hour	.0985
End of third hour	.0975
End of fourth hour	.0965
End of fifth hour	.0955
End of sixth hour	.0945
End of seventh hour	.0935
End of eighth hour	.0930

EXPERIMENT ILLUSTRATING USE OF SIMPLE PERVERS CATHODES.

An experiment was undertaken to show the recovery of silver and of cyanide of potassium from a rich solution. Only four simple pervers cathodes were used. The current gap was half an inch. The total length of electrodes in the box was 9½ inches, and the

active cross section of the cathodes was 1 square decimeter, or one-ninth square foot, which is the active cross section of the electrodes in the following experiments.

The precipitation in four hours was 92.24 per cent of the silver, whereas the cyanide content increased by 0.090 per cent. A deposition box constructed on the same scale and holding 1 ton of solution, at the same rate, would have treated 36 tons in 24 hours, and would have precipitated 92.24 per cent of the silver.

RECOVERY OF CYANIDE.

The experiment was conducted with four simple pervious cathodes each 1 inch thick, and with a half-inch current gap. The cathodes were of excelsior charcoal and had a total nominal area of 8 square decimeters, or eight-ninths square foot, but the actual surface area, which was incalculable, was much greater. The rate of flow was 2.4 liters per minute. The current density was less than 2 amperes per square foot. The solution was one of KAgCy_2 , and contained 24 grams of silver. The results are shown in the following table:

Results showing the progressive regeneration of cyanide.

Hours.	Volts.	Amperes.	Silver content.		KCy per cent.
			Mg. per 100 c. c.	Ounces per ton.	
0	3.5	2.0	120.15	35.06	0.099
1	3.5	1.9	95.68	27.89	.118
2	3.5	2.15	68.26	19.90	.140
3	3.5	2.32	37.19	10.85	.168
4	3.5	2.25	9.48	2.77	.188
5	3.5	2.2	1.15	.34	.182
6	3.5	2.05	.08	.02	.170
7	3.5	2.00	.02	.006	.154

The preceding table shows that the most economical point at which to stop the precipitation was reached in four hours, for at that time, with only four cathodes, 92.24 per cent of the silver was precipitated and the cyanide had increased from 0.099 per cent to 0.188 per cent, or about 90 per cent. The amount treated was 20 liters, or 6 times the volume of the box, giving a capacity of 36 tons per 24 hours for a 1-ton box. A further analysis of the results of the above experiment is shown in the following table:

Analysis of results of experiment with simple pervious cathodes.

Time, hours.	Volume of solu- tion treated, liters.	Silver deposited.		Theoreti- cal weight of silver depos- ited, grams.	Ampere hour effi- ciency, per cent.	KC _y , per cent.	KC _y , gain or loss.	
		Mg. per liter.	Grams.				Hourly, grams.	Total gain or loss, grams.
1	19.79	244.7	4.843	1.95	7.868	61.53	+0.019	+3.79
2	19.68	274.2	5.369	2.005	8.070	66.70	+.022	+4.33
3	19.57	310.7	6.081	2.235	9.018	66.73	+.028	+5.48
4	19.46	277.1	5.391	2.285	9.220	57.58	+.020	+4.28
5	19.35	83.3	1.612	2.225	8.978	17.95	-.006	-1.16
6	19.24	10.7	.206	2.125	8.574	2.40	-.012	-2.31
7	19.13	.6	.011	2.025	8.171	.13	-.016	-3.06
								+17.88
								- 6.53

The preceding table shows that the ampere-hour efficiency is high for the first four hours, and that if the action had been stopped 92.24 per cent of the silver would have been recovered. The efficiency of silver deposition was still fair in the fifth hour. For the entire seven hours the silver precipitation was 99.98 per cent. The last two or three hours are seen to have been wasteful of the electric current. The increase in current at constant voltage is probably brought about

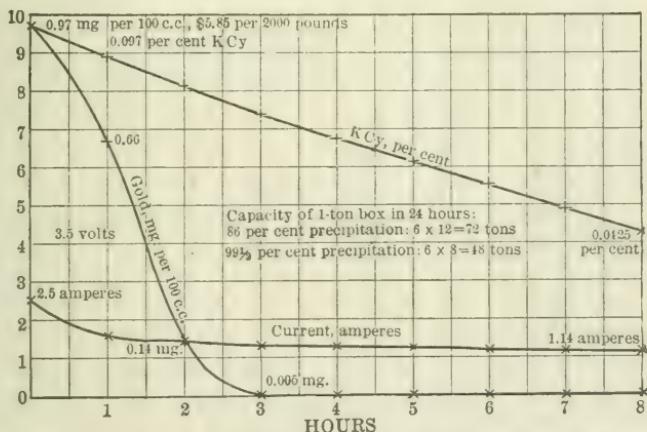


FIGURE 36.—Electrodeposition results with moderately rich gold solution; 4 simple pervious cathodes, each 1 inch thick and containing 14 grams "excelsior" charcoal, and 5 Acheson-graphite comb anodes, each with 4 4-inch rods. Length of box occupied, 9 $\frac{1}{2}$ inches, cross section 1 square decimeter, 8 cathode faces. Voltage, 3 $\frac{1}{2}$, $\frac{1}{2}$ -inch current gap. Solution, 20 liters, contained 20 grams KC_y, 20 grams KHO, 194 mg. Au as KAuCy₂. Rate of flow, 3 liters per minute. Compare with fig. 37.

by increased conductivity of the charcoal due to the deposited metal on it, and the final fall marks the point when the silver was nearly all deposited from solution.

TREATMENT OF A GOLD CYANIDE SOLUTION OF MODERATE RICHNESS.

An experiment was conducted with gold cyanide solution instead of silver cyanide solution, but all other conditions were identical

with the preceding one. The original content of the solution was \$5.85 in gold a ton. The results are shown in figure 36 and in the following table:

Results of experiment with gold solution.

Hours.	Volts.	Amperes.	Gold, milligrams per 100 c. c.	Gold per ton.	KCy, per cent.
0	3.5	2.5	0.97	\$5.85	0.097
1	3.5	1.6	.06	4.02	.089
2	3.5	1.47	.14	.81	.081
3	3.5	1.33	.005	.03	.0735
4	3.5	1.29	Trace.	Trace.	.0675
5	3.5	1.25	Trace.	Trace.	.061
6	3.5	1.19	Trace.	Trace.	.0545
7	3.5	1.13	Trace.	Trace.	.0485
8	3.5	1.14	Trace.	Trace.	.0425

Evidently there was no advantage in continuing after the first three hours, as 3-cent tailings are sufficiently low. While a regeneration of cyanide is possible from rich silver solutions, it is not usually possible with such gold solutions as occur in practice. A steady loss

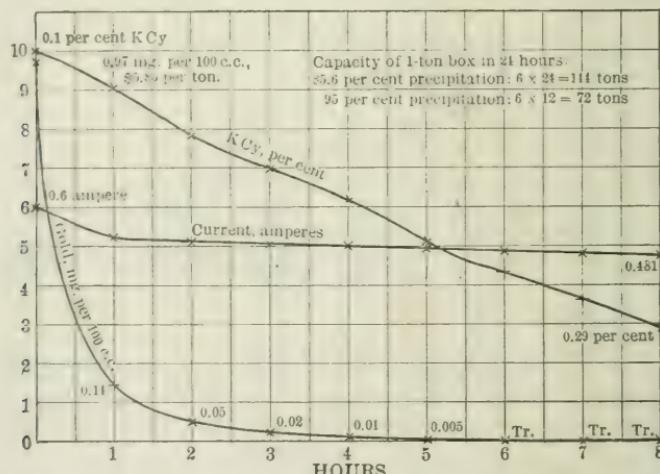


FIGURE 37.—Electrodeposition results with moderately rich gold solution; six compound pervious electrodes, each 1 inch thick and containing 14 grams "excelsior" charcoal, and 1 Acheson-graphite anode. Length of electrodes, 9½ inches; six cathode faces; six ½-inch current gap at 3.5 volts, 21 volts in all. Solution and rate of flow, same as in fig. 36.

of cyanide occurs with these, nearly proportional to the time, but increasing somewhat with the decrease of gold.

EXPERIMENT WITH USE OF COMPOUND PERVERIOUS ELECTRODES.

A duplicate of the preceding experiment in all conditions other than that compound pervious electrodes were employed was next conducted. (See fig. 37; compare with fig. 36.) The five compound

pervious cathodes were each 1 inch thick. The length of the electrodes in the box was $9\frac{1}{2}$ inches. In this experiment there were only six cathode faces instead of eight, as before. The current gap was one-half inch. The six current gaps at $3\frac{1}{2}$ volts amounted to 21 volts. In three hours 98 per cent and in four hours 99 per cent of the gold was precipitated at a capacity of 24 tons per 24 hours in a 1-ton box.

\ RECOVERY OF SILVER AND REGENERATION OF CYANIDE.

A similar experiment was further undertaken to illustrate the recovery of silver and also the recovery of cyanide. In the experiment six compound pervious electrodes were used, each 1 inch thick and containing 14 grams of charcoal, and one simple pervious Acheson-graphite anode. The six current gaps were one-half inch each. The length of box was $9\frac{1}{2}$ inches, and the solution was 20 liters in volume, containing 20 grams KCy, 20 grams KHO, and silver in the form of KAgCy_2 . The results were as follows:

Results of experiment to show recovery of silver and cyanide regeneration.

Hours.	Volts.	Ampere.	Silver.		KCy, Per cent.
			Milligrams per 100 c.c.	Ounces per ton.	
0.....	21	0.730	125.29	36.6	0.0985
1.....	21	.709	86.97	25.37	.1210
2.....	21	.691	44.86	13.01	.1570
3.....	21	.622	16.21	4.72	.1795
4.....	21	.590	1.68	.48	.1830
Added KAgCy_2	21	.820	126.95	37.00
5.....	21	.820	79.60	23.21	.219
6.....	21	.813	30.36	8.85	.252
7.....	21	.759	5.38	1.57	.251
8.....	21	.740	.38	.11	.236

The table shows that during the first four hours there was recovered 98.69 per cent of the silver from the 36.6 ounces present and 0.0845 per cent of the KCy, not allowing for samples. During the second four hours 99.7 per cent of the silver was recovered from the 37 ounces present, and 0.053 per cent of the KCy.

EFFECT OF CURRENT GAP.

Some experiments were undertaken to determine the effect of current gap upon capacity. In these tests the electrodes were one-half inch thick and were filled with excelsior charcoal. In the experiment in which, for example, the current gap was one-half inch, each box was one-half inch thick, being filled with charcoal filaments, and had on the outside a one-fourth inch cover, in such a way that two of these one-fourth inch covers were face to face, making a

current gap of one-half inch. The maximum capacity for a 95.5 per cent precipitation with one-half inch current gaps was found to be only 48 tons for a 1-ton box in 24 hours. With the one-fourth inch current gap the maximum capacity for 95.8 per cent precipitation was 144 tons, or nearly three times as great. The length of electrodes in these experiments was $9\frac{1}{2}$ inches. There were in the first experiment eight current gaps of one-half inch at $3\frac{1}{2}$ volts, making a total of 28 volts. In the second experiment there were 11 current gaps of one-fourth inch each at $3\frac{1}{2}$ volts, making a total of 38 volts.

The results of the two experiments, for which curves of precipitation are shown in figures 38 and 39, are well worth careful study and comparison. I strongly advise that the attempt be made to use the smaller current gap wherever it is possible to do so.

EFFECT OF LIME ON SILVER PRECIPITATION.

An experiment was conducted to determine the effects of lime on the precipitation, the solution containing cyanide of silver and free KCy. Compound pervious electrodes were used and one simple pervious Acheson-graphite comb anode. There were 11 cells, each one-half inch thick, and 11 one-quarter-inch current gaps of $3\frac{1}{2}$ volts each, giving $38\frac{1}{2}$ volts for the 11 boxes. The 20 liters of solution contained 20 grams of KCy, and 10.2 grams of CaO, together with 24.43 grams of silver as KAgCy_2 . No caustic soda or potassa was present. The precipitation was 93.5 per cent complete at the rate of 144 tons per 1-ton box for 24 hours, and 99.5 per cent complete at the rate of 72 tons per 1-ton box in 24 hours. The results are shown in figure 40.

It is evident from the fall in the content of protective alkali that the caustic lime was partly converted into cyanide of calcium. It was noticed, further, that the fall in protective alkali was coincident with the rise in free cyanide, and that when the silver cyanide ceased to be precipitated the protective alkali remained nearly constant. When a new charge of cyanide of silver was added the protective alkali again fell and the free cyanide increased. The regeneration of free cyanide, in short, was at the expense of the protective alkali. These results are shown by the curves in figure 40. No remark need be made other than that needed to call attention to the rate of precipitation, which was 93.5 per cent in one hour, whereas the capacity was at the rate of 144 tons a day. Furthermore, at the rate of 72 tons a day, 99.5 per cent precipitation was obtained.

SIMPLE PERVIOUS CATHODES WITH SILVER CYANIDE AND LIME.

A test was made in which there were employed six simple pervious charcoal cathodes and six simple pervious Acheson-graphite comb

anodes as electrodes; 20 liters of solution containing 20 grams KCy, 9.52 grams CaO or 0.476 per cent CaO, 38.714 grams silver in the form of KAgCy_2 , and current gaps of one-fourth inch and a voltage

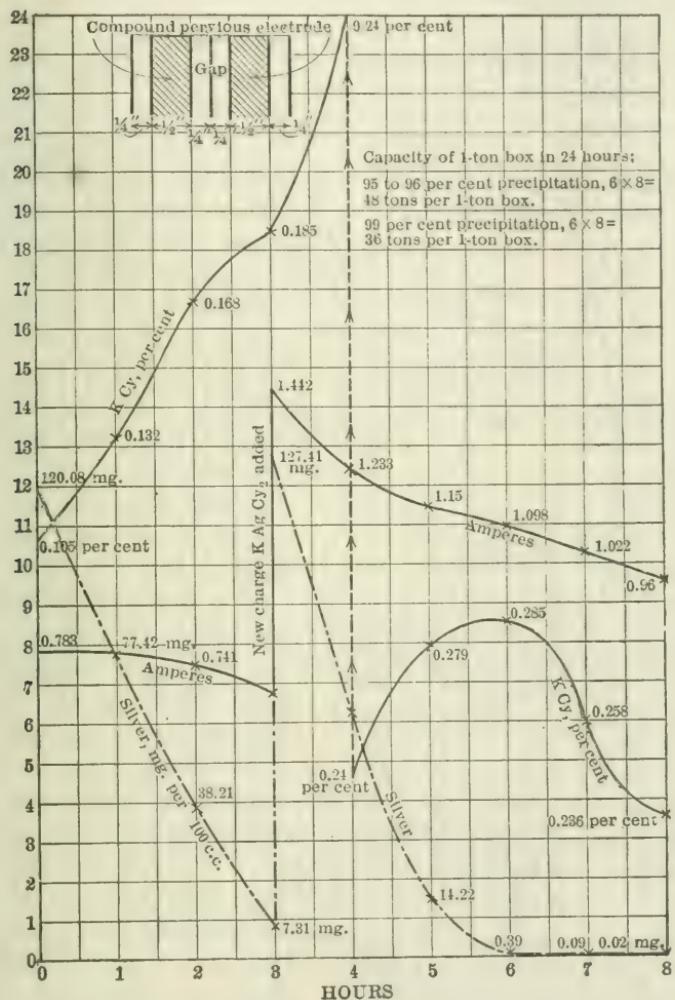


FIGURE 38.—Electrodeposition results with rich silver solution, using $\frac{1}{4}$ -inch current gaps. Eight compound pervious charcoal electrodes, each one-half inch thick; length of box occupied, $9\frac{1}{2}$ inches; cross section, 1 square decimeter. Eight current gaps at $3\frac{1}{2}$ volts, 28 volts in all. One Acheson-graphite comb anode. Solution, 20 liters, contained 20 grams KCy, 20 grams KHO, and 24.016 grams Ag as KAgCy_2 . Rate of flow not recorded; high. Note gain in KCy while Ag is being precipitated; loss afterwards

of $3\frac{1}{2}$. The cross section of the box containing the electrodes was 1 square decimeter, and the total length was $9\frac{1}{2}$ inches.

On plotting the results it was found that the amount of silver in solution closely followed the protective alkalinity. Thus as the

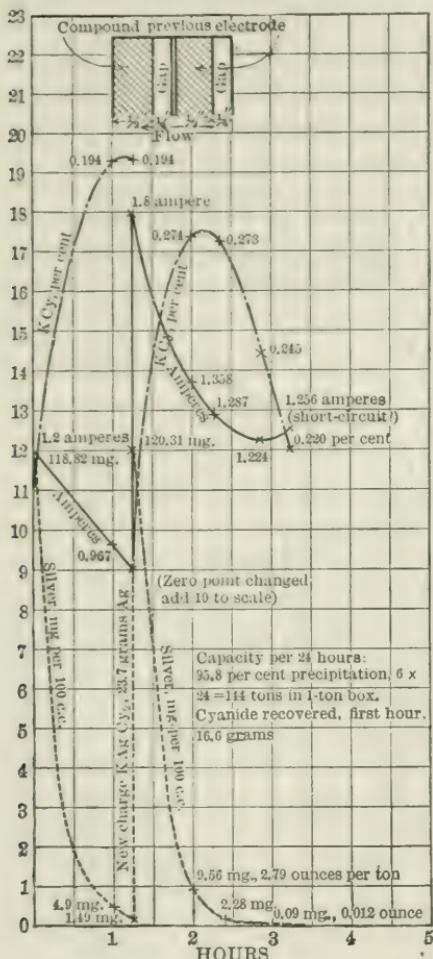
silver is removed the content of protective alkali diminishes, while at the same time the free cyanide increases. Certain irregularities in the conditions of test, due to the lack of sufficient free cyanide of potassium to keep in solution all the silver cyanide that was deposited on the anodes, caused resistances that made the current irregular. The blowing out of a fuse also caused some irregularity, and it is probable that there was some variation in the amperes, due in part to short circuits. However, the precipitation from the rich solution, notwithstanding these irregularities, was found to be very satisfactory.

In four hours the precipitation was 99.74 per cent, the capacity being at the rate of 36 tons for a 1-ton box in 24 hours. For a three-hour period the precipitation was 92.85 per cent, the capacity being at the rate of 48 tons per day for a 1-ton box.

The solution employed was probably as rich as would ever have to be precipitated in practice. Each of the six electrode boxes held 4.66 grams of excelsior charcoal, or 28 grams in all. The ash from this charcoal, including the silver, the lime, etc., weighed 47.59 grams. After the soluble salts were removed with dilute hydrochloric acid the residue—silver and insoluble silica—weighed 39.35 grams as against 38.714 grams of silver contained in the original solution. Hence there was soluble in hydrochloric acid 8.24 grams of substance, including the hydrates and carbonates of lime and potassa and the soluble constituents of the ash.

FIGURE 39.—Electrodeposition results with rich silver solution, using $\frac{1}{4}$ -inch current gaps. One Acheson-graphite anode, 10 compound pervious charcoal electrodes, $9\frac{1}{2}$ inches long; cross section, 1 square decimeter; 1 simple pervious charcoal cathode. Eleven current gaps, at $3\frac{1}{2}$ volts, or $38\frac{1}{2}$ volts in all. Solution, 20 liters, contained 20 grams KCy, 20 grams KHO, 23.7 grams Ag as KAgC_2 , and no lime. Electrodes choked with silver; grade increased from $\frac{1}{4}$ inch to $1\frac{1}{4}$ inches per foot; rate of flow cut from 3.5 to 0.2 liters per minute (210 to 150 per hour); velocity, 13.8 to 7.9 inches per minute. Note increase in capacity compared with fig. 38.

cluding the hydrates and carbonates of lime and potassa and the soluble constituents of the ash.



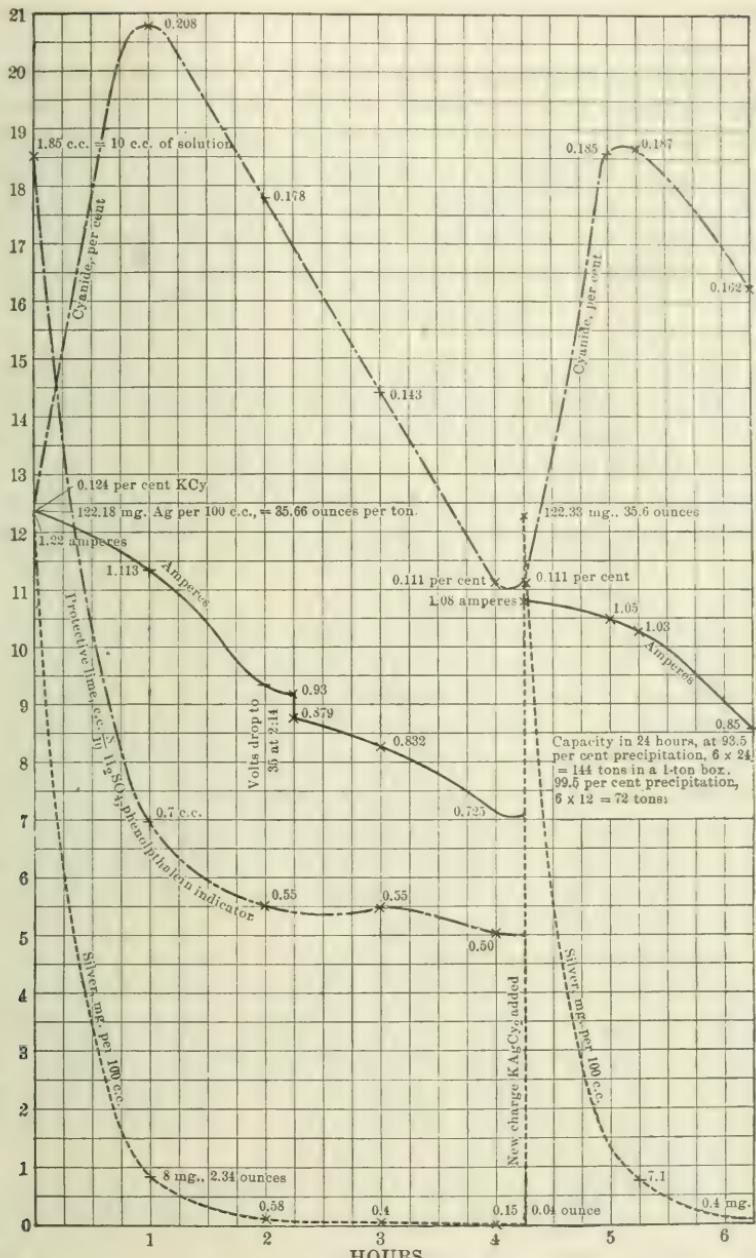


FIGURE 40.—Electrodeposition results showing effect of lime on the precipitation. One simple and 10 compound porous electrodes, each one-half inch thick and containing 9½ grams charcoal, 104 grams in all. Eleven one-fourth-inch current gaps at 3½ volts, 38½ volts in all. Solution, 20 liters, contained 20 grams KCy, 10.2 grams (0.051 per cent) CaO, and 24.43 grams of silver as KAgC_2 ; 24.43 grams of silver as KAgC_2 was added at 4½ hours; no NaHO used. Rate of flow, 5 liters per minute; velocity, about 19.7 inches per minute.

PRECIPITATION OF GOLD FOLLOWING THE PRECIPITATION OF SILVER.

An interesting experiment was made in which two successive charges, the first of silver cyanide and the second of gold cyanide, were treated in the same box. The electrodes were already coated with silver and therefore were in excellent condition for conducting the current and depositing the gold, which was added from a cyanide solution containing \$24.36 per ton. In one hour 98.27 per cent of the gold was precipitated, the capacity for a 1-ton box being at the rate of 112 tons per 24 hours. The results are shown in Plate V.

It is evident from the precipitation curves that no good purpose was served in continuing the precipitation more than two hours, for when this was done cyanide was lost and little gold precipitated. The precipitation curves are found to be all logarithmic ones, and the precipitation extremely rapid at first, but slow toward the last. The economical period of the precipitation is therefore the first few hours, and this factor should be made use of to the fullest extent possible.

In conducting the experiment one simple pervious charcoal anode with graphite rod was used and 13 compound pervious electrodes, each containing 10 grams of excelsior charcoal. A cathode of the simple-pervious type containing 8 grams of excelsior charcoal was used. There were 14 current gaps, each one-fourth inch. The voltage between electrodes was $3\frac{1}{2}$ and the total voltage 49. The electrodes were 1 square decimeter in area and the length of the box 13 inches. The solution, 20 liters in volume, contained 20 grams NaHO, 20 grams KCy, 24.07 grams silver as KAgCy_2 . The rate of flow was 13.8 inches per minute.

At the end of one hour 87.2 per cent of the silver was precipitated. Hence the capacity of the box for a 1-hour treatment is 4.67 times 24, or 112 tons for a 1-ton box in 24 hours. In 1 hour and 30 minutes there was 98.70 per cent precipitated; the capacity was 4.67 times 18 or 84 tons for a 1-ton box. In two hours 99.78 per cent was precipitated, hence the capacity for a 2-hour treatment was 4.67 times 12, or 56 tons for a 1-ton box.

At the end of this experiment 0.808 gram of gold in the form of KAuCy_2 and 0.685 gram of silver as KAgCy_2 were added to the solution without removing the electrodes and the current was started as before. The remarkably good results shown for gold are probably due to the fact that the cathodes were already coated thoroughly with metallic silver, which made them an excellent conductor and facilitated the precipitation of the gold.

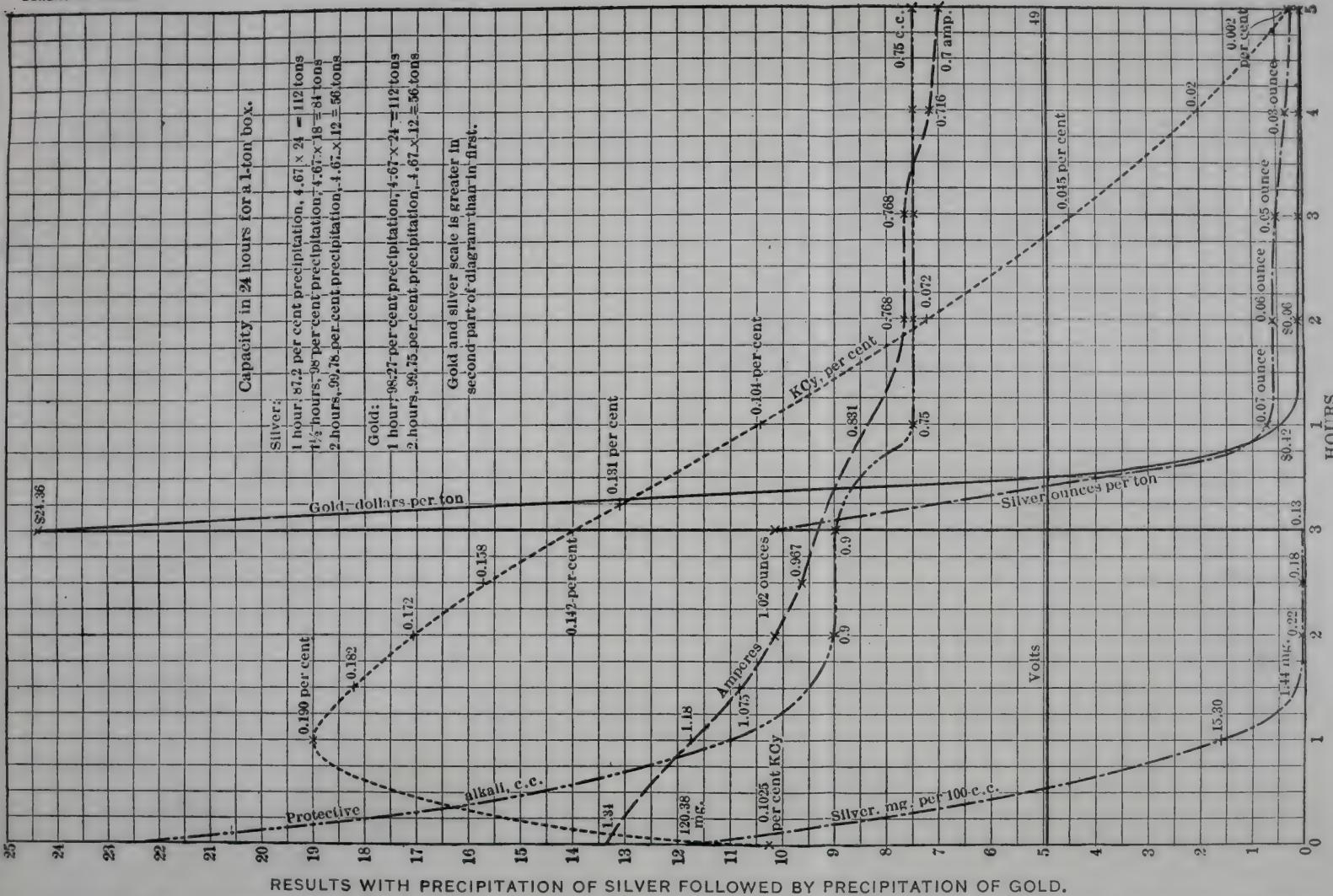
In the first hour there was precipitated 98.27 per cent of all the gold present. Hence the capacity of the box, which contains 4.28

Capacity in 24 hours for a 1-ton box.

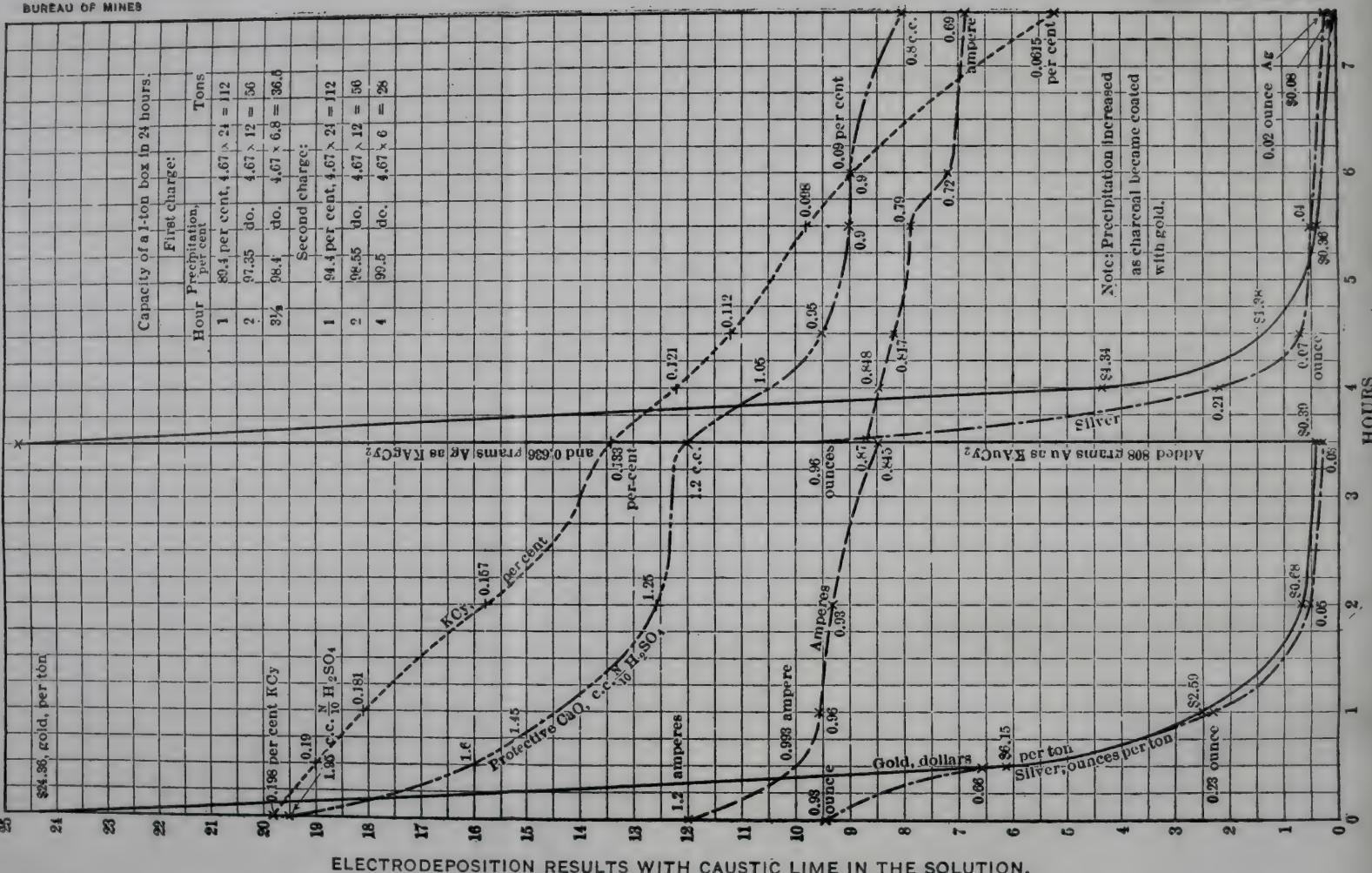
Silver:
 1 hour, 87.2 per cent precipitation, $4.67 \times 24 = 112$ tons
 $1\frac{1}{2}$ hours, 98 per cent precipitation, $4.67 \times 36 = 170$ tons
 2 hours, 98.75 per cent precipitation, $4.67 \times 48 = 228$ tons

Gold:
 1 hour, 98.27 per cent precipitation, $4.67 \times 24 = 112$ tons
 2 hours, 98.75 per cent precipitation, $4.67 \times 48 = 228$ tons

Gold and silver scale is greater in second part of diagram than in first.

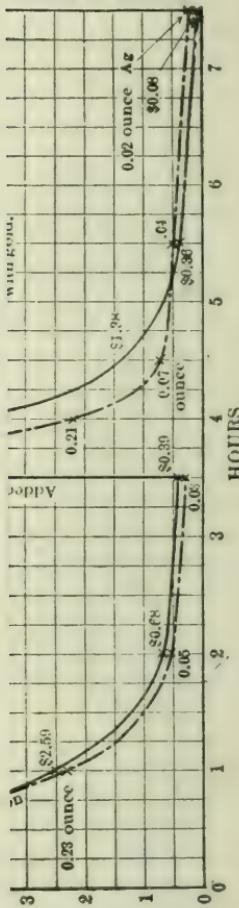


One Acheson graphite anode; 13 compound and 1 simple charcoal electrodes, each $\frac{1}{2}$ inch thick; length of box occupied, 12 inches; cross section, 1 square decimeter. Fourteen $\frac{1}{4}$ -inch gaps at $3\frac{1}{2}$ volts, or 49 volts in all. Rate of flow, 3.6 liters per minute; velocity, 13.8 inches per minute. Solution, 20 liters, contained 20 grams KCy, 20 grams NaHO, 24.07 grams, Ag. as KAgC_2 , and no lime.



One simple anode, 13 compound electrodes, and 1 simple cathode, all of excelsior charcoal in boxes $\frac{1}{2}$ inch thick. Fourteen $\frac{1}{4}$ -inch current gaps at $3\frac{1}{2}$ volts each, or 49 volts in all. Solution, 20 liters, contained 40 grams KC_y , 10.92 grams CaO , 0.808 gram gold as KAuC_y , 0.636 gram silver as KAgC_y , and no KHO or NaHO . Rate of flow, not recorded, high.

BULLETIN 150 PLATE VI



t gaps at $3\frac{1}{2}$ volts each,
 AgC_2 , and no KHO or

liters, would be 4.67 times 24, or 112.08, tons for a 1-ton box in 24 hours. At the end of the first two hours 99.75 per cent of the gold was precipitated, making the capacity of the box equal to 4.67 times 12, or 56.04, tons for a 1-ton box in 24 hours. It will be noticed that there was no advantage in running after the first two hours, as the amount of gold left at the end of that time was only 6 cents per ton. This content was reduced in the full three hours to 1½ cents, but it was accomplished at the cost of destroying the total remaining cyanide. The desirable point at which to stop the precipitation is thus seen to have been probably after the first or second hour.

THE DIRECT USE OF A 110-VOLT CIRCUIT.

An experiment was undertaken to illustrate a mode of utilizing a 110-volt circuit, in which, for the purpose, two 13-inch boxes such as I have described were placed in series. These were given, in the first part of the experiment, a total tension of 98 volts, having altogether 28 current gaps at $3\frac{1}{2}$ volts each. The result, as regards precipitation, was very satisfactory. During the first half hour there was precipitated 93 per cent of the silver, giving a capacity of 112 tons for a 1-ton box. At the end of the first hour 99.8 per cent was precipitated.

The positive current was introduced by a simple pervious anode. Its course was through 13 compound pervious electrodes, out through a simple pervious cathode to a simple pervious anode at the head of the second box, and thence through 13 compound pervious electrodes to a simple pervious cathode. To adjust the voltage a resistance similar to that shown in Plate IV, A, containing twenty 32-candlepower incandescent lamps connected in parallel, was put in series with the cells. As there were 28 current gaps in the two boxes at 3.5 volts, the total voltage was 98 volts.

In starting the experiment, all of the twenty 32-candlepower lamps, connected in parallel, were placed in series behind the box. This gave at the start 98 volts. First one and then a second of these lamps, and so on, were disconnected, to adjust the voltage and to produce the effect wanted. The total length of electrodes in the two boxes was 24 inches; the current gaps were each one-fourth inch. Twenty liters of solution, containing 20 grams KCy and 20 of KHO, was used. The results are shown in figure 41.

In the first half hour, at 98 volts, 93 per cent of the silver was precipitated, the capacity being equivalent to 112 tons for a 1-ton box for 24 hours. At the end of the first hour, at 98 volts, 99.8 per cent was precipitated, the corresponding capacity being 56 tons for a 1-ton box in 24 hours. During the second hour, at 60 volts, 98 per cent was precipitated, and the capacity would be 56 tons for a 1-ton box. The

rate of precipitation, however, had nearly reached the maximum, with the 60-volt charge, at the end of the fourth hour, then fell slightly below 96 per cent in one hour, but at the end of the sixth hour was 99.85 per cent.

PRECIPITATION OF RICH GOLD AND SILVER SOLUTIONS IN THE PRESENCE OF LIME.

An experiment was undertaken to determine the effect of caustic lime (CaO) on the precipitation both of gold and silver from strong cyanide solutions. The results are shown in Plate VI.

The solution contained about $1\frac{1}{4}$ ounces of gold and 1 ounce of silver. A single box with 14 one-fourth inch current gaps was used. The results are to be compared with those shown in figure 41, where the precipitation was more rapid on account of the electrodes having been previously coated with silver and on account of the absence of lime.

In treating such rich solutions there is no necessity of reducing the gold content much lower than 90 per cent, as the solution is used over and over again. The presence of a small amount of gold in the leaching solution has no bad effect on the extraction. The most economical results are obtained in that way. A careful examination of the curves shows the point at which to stop in any given experiment.

The 13-inch box contained 1 simple pervious anode, 13 compound pervious electrodes, and 1 simple pervious cathode. Each of the 15 electrode boxes contained 10 grams of excelsior charcoal. The total length of electrodes was 12 inches, the cross section being 1 square decimeter, or one-ninth square foot. The 14 current gaps, of one-fourth inch each, at 3.5 volts, required 49 volts. Twenty liters of solution were treated, containing 40 grams of KCy , 0.808 gram of gold as KAuCy_2 , 0.636 gram of silver as KAgCy_2 , and 10.92 grams of CaO .

During the first hour 89.4 per cent of the gold was precipitated, in which time the box treated 4.67 times its content of solution, making the capacity equivalent to 112 tons in 24 hours for a 1-ton box. During the second hour 97.3 per cent of the gold was precipitated, giving a corresponding capacity of 56 tons. At the end of three and one-half hours 98.4 per cent of the gold was precipitated, the capacity corresponding to this rate being 36.5 tons. The second charge was treated four hours, in which time the gold precipitation was 99.5 per cent. The corresponding capacity of a 1-ton box would be 28 tons of solution in 24 hours.

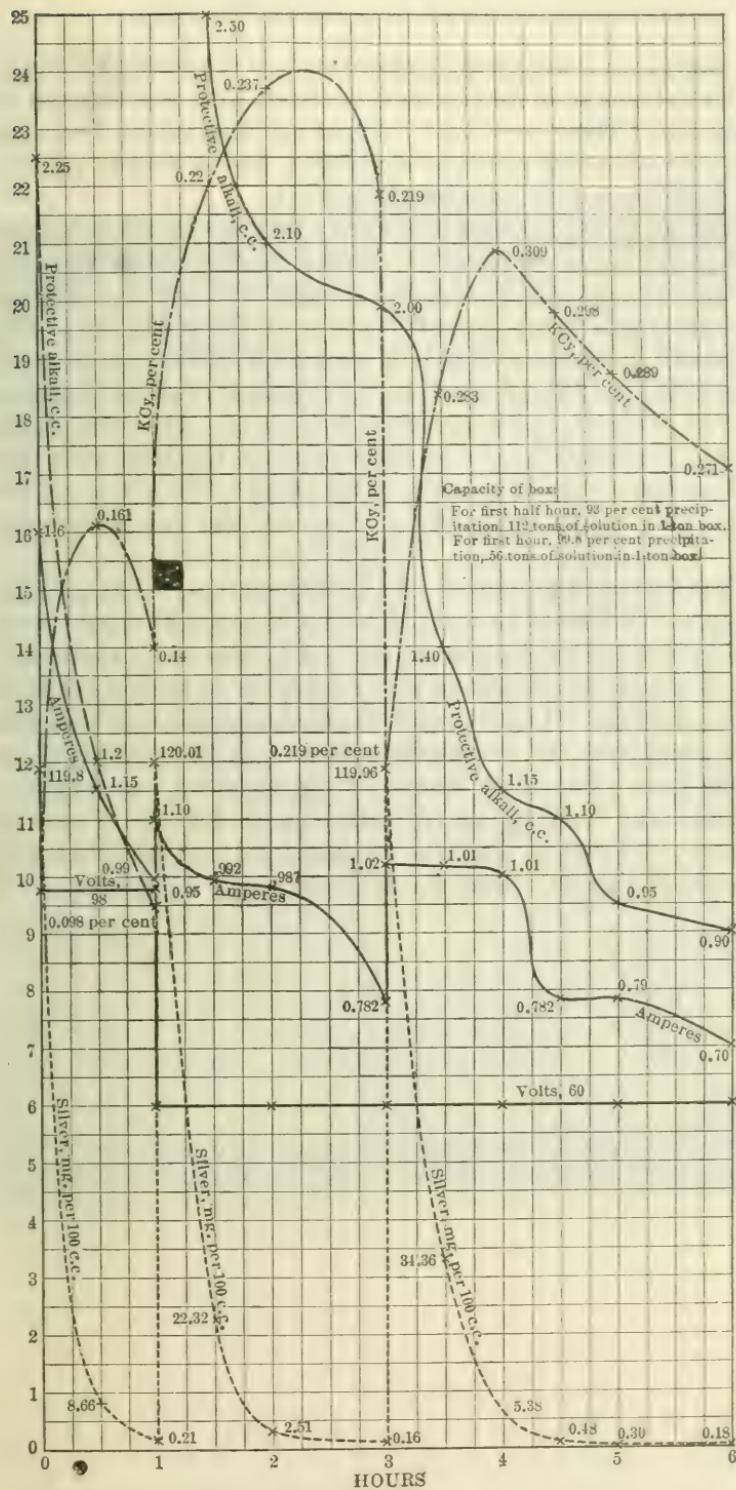


Figure 41. Electrodeposition results with 110-volt direct-current circuit as source of power. Two electrode boxes in series, each having 1 simple porous anode and 13 compound porous and 1 simple previous cathode. Voltage regulated by bank of lamps. Twenty-eight currentamps; mean current drop from box to box for first hour, $98 \div 28 = 3.5$ volts; for rest of test $60 \div 28 = 2.22$ volts. Silver solution, 20 liters, contained 20 grains KCY and 20 grains KIO_4 . Rate of flow not recorded.

EXAMPLE OF CLEAN-UP FROM SILVER SOLUTIONS.

Three charges of silver of 23.59 grams each in the form of KAgCy_2 , making a total charge of 70.77 grams of silver, were run through the deposition box. There were used 1 simple pervious anode of excelsior charcoal, 13 compound pervious electrodes, and 1 simple pervious cathode, each containing 8 grams of charcoal.

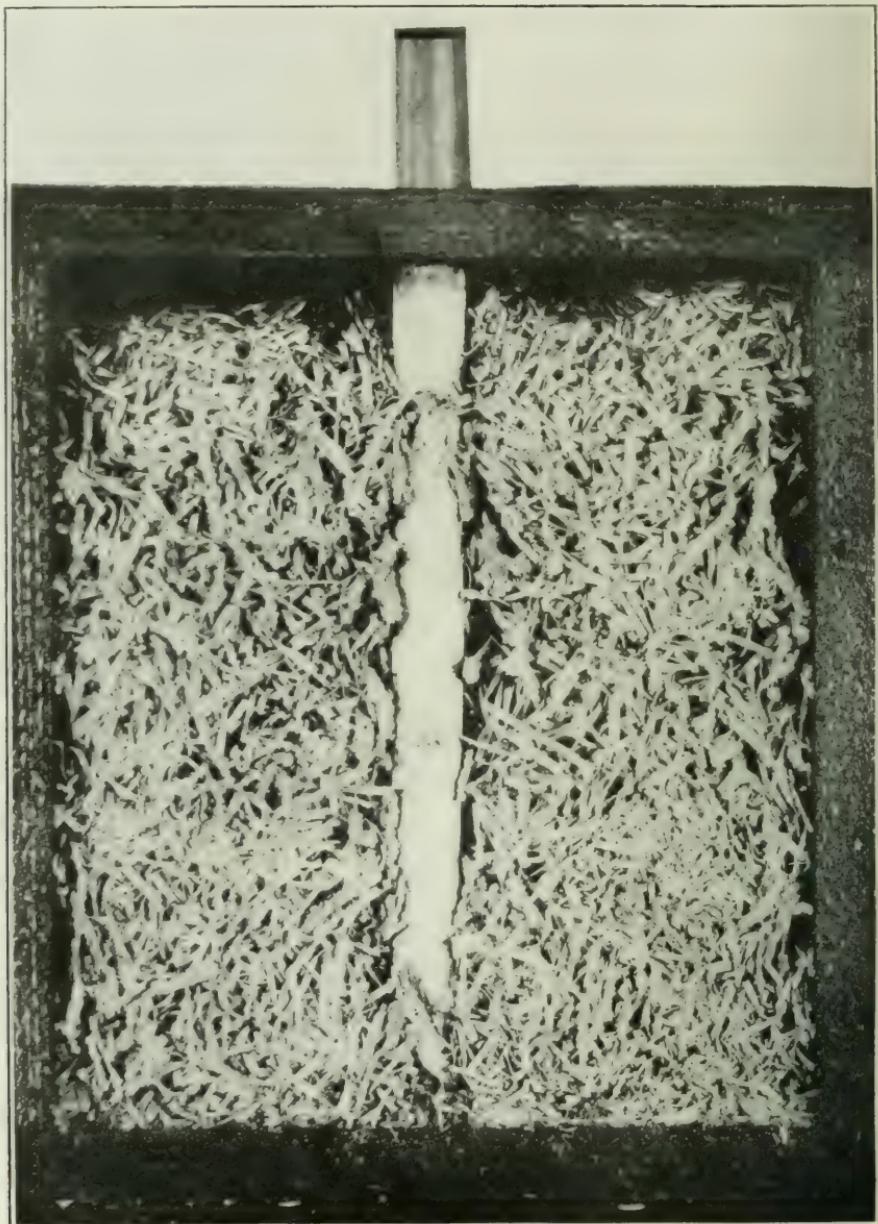
The solution after treatment contained 0.63 mg. silver per 100 c. c., there being left in the 20 liters of solution 0.126 grams. The charcoal of the cathode was thoroughly gorged with silver. The upstream or cover side of the cathode is shown in Plate IV, *B* (p. 143), the cheesecloth being covered with a mass of pure crystals of silver. The deposit had so extended that there was danger of short-circuiting.

Plate VII shows the reverse side of this cover. Here the cheesecloth is seen to support a mass of silver crystals, together with fragments of excelsior charcoal, coated with silver. The silver on this cover was very easily removed by scraping and brushing under water.

Plate VIII shows the interior of the cathode box. The graphite conducting rod is seen to be covered with a loosely adhering coating of silver crystals. The charcoal in the box is seen to be thoroughly coated with silver, the weight of silver being more than three times that of the charcoal. The charcoal in the compound pervious electrodes, as usual, was not so densely plated as at the cathode at the end of the box. The total result of the clean-up, consisting of 70.644 grams and 4.956 grams of ash, was as follows: From the simple anode, 25.3 grams; from the 14 compound pervious electrodes, cathode side, 46.2 grams; from the 14 anode sides, 4.1 grams.



BACK OF COVER. SIMPLE PERVERS CATHODE NEARLY CHOKED WITH SILVER.



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